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ABSTRACTS OF PAPERS.

Section of Chemistry.

*President :—Professor S. S. Bhatnagar, D.Sc.*

A handwritten signature in black ink, consisting of a large, stylized 'C' followed by a series of loops and a final vertical stroke.

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.





charge when similarly treated. Dehydrated substances like the above adsorb their constituent ions very strongly whereas hydrated substances adsorb any ions without showing any strong preference for the constituent ions. Irreversible coagulation and charge reversals can also be satisfactorily explained on the above basis of adsorption by hydrated substances. Generally on coagulation, a hydrated colloid like stearic acid becomes dehydrated and loses its power of adsorbing ions from neutral salt solutions, and consequently the coagulation is irreversible.

### 13. Alco-Gel of silica.

BASRUR SANJIVA RAO *and* K. G. DOSS.

Adsorption by silica gel is ordinarily dependent on the water envelope in it; attempts have been made to obtain gel with an alcohol envelope. Experiments on the complete replacement of the water by alcohol, carried out by Graham, by Patrick, and by Fells and Firth give contradictory results. The authors of this paper have extracted with hot alcohol, silica gel (placed in a Jena glass thimble) in a Soxhlet apparatus, the alcohol in the flask being kept anhydrous by addition of metallic calcium and barium oxide. On prolonged treatment the water in the gel was found to be about 1% by organic combustion methods suitably modified. Replacement of water was also attempted by a dynamic method in an apparatus in which air was continuously circulated in a closed system through anhydrous alcohol and the gel.

Adsorption curves for silica gel and water alcohol mixtures indicate that replacement of water becomes progressively difficult with decrease in water content of the gel. The authors tentatively conclude that complete replacement of water though it may not be impossible, is extremely difficult to effect.

### 14. Adsorption by silica gel from binary mixtures of liquids.

BASRUR SANJIVA RAO *and* H. M. CHANNABASAPPA.

Silica gel particles have a water envelope, and B. S. Rao (Thesis, London University, 1926) has shown that selective adsorption from binary mixtures of liquids is dependent on the energy of the interface that this water envelope forms with each of the two liquids. The interface between water and carbon tetrachloride has the same energy as that between water and carbon disulphide. The authors of this paper have determined at 30°C, adsorption by silica gel from mixtures of carbon tetrachloride and carbon disulphide in different concentrations and find in conformity with the above view, no selective adsorption.

Determinations were carried out in two ways: by a static method in which the gel was treated with liquid mixtures in a thermostat and by a dynamic method in which air bubbled through the liquid and passed over the gel in a closed system, the circulation of air being effected by a double action pump of special design, working in an air thermostat and consisting of two pulsating mercury columns and four mercury valves. A Pulfrich refractometer was employed for the analysis of the mixtures.

### 15. Application of the Donnan membrane equilibrium to the determination of adsorption of ions.

S. KRISHNAMURTI *and* P. B. GANGULY.

A method is described by which the amount of hydrogen ions from hydrochloric acid adsorbed by specially prepared colloidal silicic acid is measured by using the Donnan membrane equation for a semipermeable membrane. In such a membrane it is supposed that a dialysable ion, through adsorption to a non-dialysable colloidal particle becomes non-



dialysable. From the Donnan equation an expression for the adsorbed quantity can be obtained, and using this expression, the quantity of adsorbed ions has been determined by measuring the membrane potential and activity of ions across the membrane.

#### 16. Adsorption of acids by silica.

M. P. LAKHANI, Karachi.

In view of the controversy between Joseph and Mukherjee (*Nature*, March 28, 1925; Jan. 2, 1926; Dec. 18, 1926) it appeared as if the method of preparing silica determined whether it would adsorb acid or not. Calcium silico-fluoride and  $\text{H}_2\text{SO}_4$  mixtures were distilled at low heat. The gas was collected under water. The precipitate of silica thus formed and dialysed for seven days did not adsorb  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  as indicated by analytical, Electric Conductivity and  $\text{PH}$  determinations.

#### 17. Alumina gel as a desulphurising agent in petroleum refining.

JOGENDRA KUMAR CHOWDHURY and RAMESH CHANDRA BAGCHI.

This paper deals with the suitability of alumina gel for removing sulphur compounds dissolved in petroleum oils by means of adsorption.

Sulphur in the oil has been estimated by the lamp method, modified to give concordant results.

Optimum conditions for the activation of the gel; e.g. temperature of roasting and moisture content have been determined. Influence of other factors such as concentration and nature of sulphur compounds in the oil, quantity of the adsorbent, size of particles and temperature of treatment on adsorption, has also been studied. Freundlich's adsorption isotherm has been found to be satisfactorily applicable.

The majority of sulphur compounds have been almost completely removed by oxidation with dry atmospheric air, using alumina gel as a catalyser and subsequent filtration through the adsorbent. This is an improvement on the present process of oxidation with sodium hypochlorite.

It has also been found that intimate mixtures of alumina gel with other adsorbents such as activated carbon or silica gel, specially the latter, mutually promote the adsorption capacity to a remarkable extent. This is similar to the action of "promoters" used in the preparation of catalysts.

#### 18. Emulsification at interfaces by an electric current.

M. P. VENKATARAMA IYER and P. B. GANGULY.

A series of measurements with various polyiodides have been made to elucidate the exact mechanism of the phenomenon of emulsification at the interface between nitrobenzene and water containing a polyiodide. It has been found that the necessary condition for this emulsification is the formation of the complex polyiodide ions both in the aqueous and the non-aqueous phases. The migration velocities of the polyiodide ions have been measured and it has been found that these ions are highly hydrated. An explanation of the emulsification effect is suggested based on the hydration of the polyiodide ions. An appreciable amount of heat is developed during the emulsification, which can be explained on the basis of the change of free energy of the water molecules at the interface.



## 19. Petrol-water emulsions.

C. VARADHAN.

An attempt has been made to prepare a stable emulsion of petrol and water containing a large percentage of petrol for use as a fuel in internal combustion engines. A premier colloid mill was used for emulsification and a number of soaps were tried as stabilizers. The highest concentration of petrol reached was 65 per cent. The time and mode of separation of petrol-water emulsions made with the various stabilizers have been studied. Both the oil in water type and the water in oil type of emulsion have been obtained with every one of the stabilizers used and the inadequacy of the modern adsorption film theory to explain this has been discussed in the light of this and other investigations. The drop numbers of the stabilizers used have been determined at three concentrations and the stabilizers have been arranged in the order of their efficiency.

## 20. Coagulation of blood and milk by electrolytes and the clotting of blood.

N. R. DHAR *and* SATYA PRAKASH, Allahabad.

1. Diluted blood and milk are more stable than concentrated blood and milk towards sodium, their coagulation by sodium citrate, sodium tartrate, sodium acetate, potassium oxalate and potassium fluoride.

2. In presence of small quantities of the above salts both blood and milk are stabilised because the adsorption of the negative ions and consequent increase in the negative charge.

3. Blood and milk behave abnormally towards dilution and a mixture of electrolytes and are likely to show the phenomenon of acclimatization.

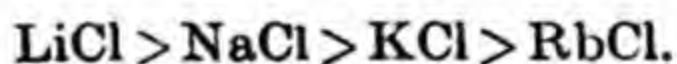
4. The clotting of blood is guided by the same laws as the formation of jellies of vanadium pentoxide, ceric hydroxide, silicic acid, etc.

## 21. The influence of electrolytes on the coagulation of ceric hydroxide hydrosol heated to different temperatures.

A. R. NORMAND *and* M. C. MUTHANNA, Bombay.

The coagulating powers of the chlorides of alkali metals and metals of the alkaline earths on positive ceric hydroxide hydrosol, heated to different temperatures, have been studied. The time required for each electrolyte to coagulate the sol was followed by means of a potassium photoelectric cell. The order of the coagulating power of the electrolyte was found to change with different degrees of dehydration of the sol.

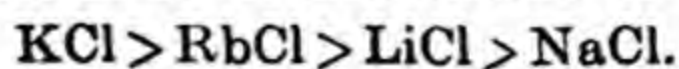
1. The order of the coagulating power of the electrolytes with sol dialysed at 28°C. is



2. With sol dialysed at 28°C. and heated to 70°C. is



3. With sol dialysed at 28°C. and heated to 100°C. is



Thus it is seen that the coagulating power of the different electrolytes depends upon the temperature condition of the sol. Thus the sol at 28°C. and 70°C. was most sensitive to LiCl and least sensitive to RbCl and KCl; but at 100°C. it was most sensitive to KCl and RbCl and least to NaCl and LiCl.



22. On the coagulation of thorium hydroxide sol by electrolytes.

B. N. DESAI.

The influence of electrolytes on colloidal  $\text{Th}(\text{OH})_4$  has been studied under different conditions.

It is observed that the Smoluchowski theory for the kinetics of coagulation holds only up to a certain concentration of the coagulator. With increase in dilution of the coagulator the coagulation velocity curves become more and more 'S' shaped and with their appearance, the Smoluchowski theory seems to be inapplicable. The 'S' shaped nature of the curves indicates that the process of coagulation is autocatalytic.

Coagulation of  $\text{Th}(\text{OH})_4$  sol by  $\text{LiCl}$  and  $\text{BaCl}_2$  has been studied with the progress of dialysis. It is found that a sol containing appreciable amounts of the peptising agent behaves abnormally to the dilution rule and that the velocity curves for equivalent concentrations of  $\text{LiCl}$  and  $\text{BaCl}_2$  are not concurrent. With the progress of dialysis the applicability of the Schulze-Hardy law increases. The abnormality to the dilution rule, as is seen from these experiments, is due to adsorption of the similarly charged ion as well as to the increase in the distance between the colloid particles on dilution of the sol and the former being the deciding factor.

Coagulation with different pairs of electrolytes has also been studied and ionic antagonism is observed in those cases where similarly charged ion is adsorbed to an appreciable extent. It is definitely seen that the antagonistic behaviour is not due to decrease in the adsorption of one precipitating ion owing to the presence of the other.

23. Studies on the formation of silver sol prepared by dispersion in the electric arc—II.

P. S. MACMAHON and S. C. VARMA, Lucknow.

In connection with the previous paper ("Action of light on silver bromide" by P. S. MacMahon and A. C. Chatterji) attempts were made to determine the properties of finely dispersed silver. A method for preparing this material was published in the meantime by Furth (Koll. Z. 34. 224, 1924) who obtained a deposit from an electric arc struck in air between silver electrodes which gave a sol on treatment with water. We have observed that this deposit is by no means pure silver: it contains large quantities of oxide and nitrate. On igniting the dust, brown fumes are given out in perceptible quantity.

The dust has been prepared by us by striking the arc between pure silver electrodes in either air, oxygen, or nitrogen. Nitrate was found to be produced in oxygen containing as little as 0.2% nitrogen. The same result was obtained in nitrogen containing a little oxygen. In pure nitrogen practically no deposit was formed and it is probable that if the gas were chemically dry there would be no formation of dispersed silver whatever.

The conditions under which the sol was produced by the addition of water to the powder was studied at length, and the results are discussed in the paper.

The properties of the solid powder were also investigated. There is evidence that this powder exposed to air or oxygen takes up a further small quantity of oxygen, indicating the oxidation of finely dispersed silver.



## 24. Sensitization of sols of prussian blue and Odèn sulphur by gelatine and tannic acid.

SATYESHWAR GHOSH.

(1) Experimental results show that a sol of prussian blue is rendered slightly unstable towards its coagulation by KCl and BaCl<sub>2</sub> in presence of gelatine. The sensitizing effect passes through a maximum and when larger quantities of gelatine are added the sol is stabilised. With HCl the sensitizing effect of gelatine is more pronounced than in cases of KCl and BaCl<sub>2</sub>.

In presence of small quantities of tannic acid prussian blue is sensitized in its coagulation by KCl, whilst there is appreciable stabilisation of the sol when coagulated by HCl.

(2) Odèn sulphur sol has been found to become unstable in presence of gelatine towards KCl and BaCl<sub>2</sub>. Odèn sulphur sol can be readily coagulated by gelatine.

Tannic acid renders Odèn sulphur sol stable towards electrolytes.

My experimental results show that Odèn sulphur sol is stabilised in presence of acid and rendered unstable in presence of alkali. Moreover, I have shown that the coagulating power of sodium and potassium salts of weak organic acids towards Odèn sulphur sol decreases with increase in their dissociation constants. These results can be explained from the point of view that pentathionic acid which is the stabilising agent in Odèn sulphur sol, is stabilised by acids and is decomposed by alkalies. Boiling renders Odèn sulphur sol unstable.

The deviation of ions of different valencies to follow the Schulze-Hardy law in the coagulation of Odèn sulphur sol is caused by the presence of acids derived from the hydrolysis of the salts.

(3) The sensitizing influence of small quantities of OH<sup>1</sup> ions in the coagulation of sols of silicic acid, tungstic acid, molybdic acid, etc., is due to the decrease in the amount of the complex negative ion present.

(4) The experimental results so far obtained by us as well as by other investigators on the sensitization of sols by gelatine, albumin, tannic acid, etc., can be satisfactorily explained from the following considerations:—

(a) Checking of hydrolysis of sols by H<sup>o</sup> ions present in the sensitizers.

(b) Charge reversal of the sensitizers due to the presence of H<sup>o</sup> ions present in the sols.

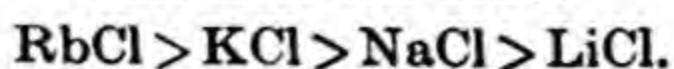
and (c) Neutralisation of charge of the sols by the oppositely charged sensitizers.

## 25. Tungstic acid hydrosol.

A. R. NORMAND and M. C. MUTHANNA, Bombay.

It is stated that tungstic acid sol is indifferent to acids, salts and alcohols. But a fairly sensitive sol has been obtained by peptising the tungstic acid both with an acid and an alkali. The sol of tungstic acid prepared in either of these ways is negatively charged and has the characteristic properties of an emulsoid sol.

The coagulating power of the electrolytes on the sol has been studied with the aid of the photo-electric cell. The order of coagulating power of the chlorides of alkali metals is of the order



The protective influence of the negative ions is as follows:—





26. On a reversible photochemical reaction between bromine and m-nitro-benzylidene malonic ester in carbondisulphide as solvent.

J. C. GHOSH, K. P. BASU and S. BHATTACHARYYA, Dacca.

The velocity of bromination of m-nitro-benzylidene malonic ester in the dark is almost nil, the reaction however, proceeds fairly quickly under strong illumination. The resulting dibromide does not decompose in the dark but with bromine as photosensitiser, dissociation of the dibromide into bromine and the original ester takes place in light. It has been found that the rate of photobromination is given by the equation :

$$\frac{dx}{dt} = k_1 I. (a-x) (b-x)$$

where  $I$  is the intensity of illumination,  $a$ ,  $b$  are the concentrations of the ester and bromine respectively. The rate of dissociation of the dibromide is given by

$$k_2 / \sqrt{I} \cdot x.$$

The observed velocity of photobromination is the difference between these two rates and is given by

$$k_1 I (a-x) (b-x) - k_2 x / \sqrt{I}.$$

The equilibrium constant

$$k = \frac{x}{(a-x) (b-x)} = \frac{k_1 I}{k_2 \sqrt{I}} = \frac{k_1}{k_2} \sqrt{I}$$

It is clear that the equilibrium constant increases as the square root of the intensity of illumination. This has been actually found to be the case.

27. The influence of the intensity of incident light on the velocity of some photochemical reactions.

B. K. MUKHERJI, Allahabad.

In all fifteen reactions have been studied from this point of view. It has been observed generally that the velocities of the reactions containing iodine as one of the reactants vary proportionally to the square root of the intensity of the incident light. Some reactions have also been noted whose velocities vary proportionally to the squares of the intensity. In 5 cases direct proportionality between velocity and intensity has been established. The variation of the velocity with the square root of the intensity of the incident light is explained by assuming that in all reactions involving iodine as the photo-active constituent, the chemical changes take place between atoms of iodine. The dependence of the velocity of the reaction between mercuric chloride and ammonium oxalate on the intensity of incident light (the former changing as the square root of the latter) is explained by supposing that photochemically the  $\text{Hg}_2\text{Cl}_4$  molecules break up into a pair of  $\text{HgCl}_2$  molecules before reacting. In general, it has been concluded that reactions which are really photochemical in nature are proportional to the square root of intensity. Whereas, those reactions which are not markedly photochemical in nature should be proportional to powers greater than unity of the incident light.

28. The action of light on silver bromide—I.

P. S. MACMAHON and A. C. CHATTERJI, Lucknow.

Pure silver bromide was sealed in a tube containing pure precipitate of gold as absorbent for bromine in an atmosphere of dry oxygen and ex-



posed to sunlight for lengthy periods. Absorption of oxygen in all cases took place in approximately the same amount as that observed in the case of silver chloride.

It is suggested by the authors that the phenomenon is not due to photochemical synthesis of an oxy-compound, but that it is due to the direct absorption of oxygen by the dispersed silver produced in the photochemical decomposition of the silver halide.

29. Oxidation of carbohydrates, fats and nitrogeneous substances by air in presence of sunlight.

C. C. PALIT, Allahabad.

1. Solutions of galactose, arabinose, cane sugar, glucose, laevulose, lactose, maltose, starch, glycogen, urea, glycine, alanine, hippuric acid, sodium urate, potassium palmitate, and potassium oxalate have been oxidised by passing air in presence of sunlight.

2. It has been found that the greater the intensity of sunlight, the greater is the amount of oxidation.

3. Zinc oxide acts as a marked photo-sensitiser in the above oxidations and in its presence the amount of oxidation in each case is greater than in its absence.

4. It is probable that by the absorption of sunlight, the cells in the animal body are activated and this activation leads to a greater amount of oxidation of fats, carbohydrates, and proteins. Hence sunlight and other kinds of artificial lights prove efficacious in the treatment of diseases specially of metabolic origin.

30. The limits of applicability of Fresnel's law and evidence in favour of surface structure from surface reflectivity.

S. S. BHATNAGAR, D. L. SHRIVASTAVA and N. G. MITRA,  
Lahore.

This paper describes an investigation on the surface structure from a study of the energy in the reflected ray from a liquid surface. The liquids examined were some organic acids, alcohols, esters, hydrocarbons and amines both in the aliphatic and aromatic series, as also some colloidal sols and solutions of inorganic substances. The limits of applicability of Fresnel's formula, calculating the energy of the reflected ray, have been explored, as it postulates uniform arrangement of molecules both in bulk and on the surface, which is contrary to Langmuir's hypothesis. It has been noticed that Fresnel's law is obeyed at higher angles of incidence of the reflected ray but at the smaller angles the variation is  $\pm 5\%$  in cases where the substances are aliphatic and have the polar groups. This may be taken as an evidence in favour of a distinct arrangement of a layer of molecules at the surface.

31. The Tesla-luminiscence spectra of Iodine and Bromine.

S. S. BHATNAGAR, D. L. SHRIVASTAVA, K. N. MATHUR and  
R. K. SHARMA, Lahore

The emission spectra of Iodine and Bromine excited by electrodeless discharge from a Tesla transformer have been examined by a quartz spectrograph. Some new bands have been noted in the ultra-violet region. The continuous back-ground has been noted to end sharply at  $\lambda$  2130 for iodine and  $\lambda$  2125 for bromine. An explanation based on the electron affinity and the dissociation potential of the molecule has been put forward.



## 32. The Tesla-luminiscence spectra of some organic solids.

S. S. BHATNAGAR, D. L. SHRIVASTAVA and R. K. SHARMA,  
Lahore.

The tesla luminiscence spectra of naphthalene, anthracene, phenanthrene, camphor, menthol, etc., have been examined with a quartz spectrograph at the ordinary room temperature.

## 33. On the possibility of isotopes in Ra emanation.

NAZIR AHMAD, Lahore.

It was noted by early workers that the period of Ra emanation, as found by the X-ray method, was generally smaller than that found by the X-ray method. It was thought by the writer that this difference was probably due to the presence of two or more isotopes in Ra emanation, their periods of decay, being a nuclear property, having different values. To test this point, two nearly equal samples of emanation, one fresh and the other old, were balanced against one another, the balance being maintained by means of a uranium resistance. The emanations were allowed to decay for several days, the balance being tested from time to time by means of the sensitive Compton electrometer. No difference in their rates of decay was observed within 1/500 which was the limit of accuracy of the experiment. The differences in the results of the early workers therefore could not have been due to the presence of isotopes but to some other hitherto unexplained cause. The experiments were performed at the Cavendish Laboratory under the guidance of Sir Ernest Rutherford.

## 34. Cosmic radiation and radio-activity.

J. M. BENADE.

Tests of the rate of discharge of an electrometer due to the presence of radio-active material in an ionization chamber was found to be unaffected by variations in the intensity of cosmic radiation. A self-recording electrometer was submerged in the Dal Lake in Kashmir.

## 35. Radio-active Columbite from Gaya district : chemical and physico-chemical examination.

N. C. NAG, Calcutta.

Complete analysis of Indian Radio-active Columbite seems not to have been attempted. The present investigation gives the proportions of the various constituents present in a sample of Gaya District Columbite, supplemented by electroscopic determination of Uranium content (and hence of Radium) by comparison with a sample of standard Joachimstahl Pitchblende (thorium free).

Specific gravity of a piece weighing 55.956 grams was found to be 5.46 with an approximate hardness of 6.

Niobium Pentoxide	..	..	..	59.05 %
Tantalum Pentoxide	..	..	..	19.85 %
Ferrous oxide	..	..	..	7.90 %
Ferric oxide	..	..	..	0.22 %
Manganous oxide	..	..	..	11.62 %
Cupric oxide	..	..	..	0.15 %
Uranium oxide $U_3O_8$	..	..	..	0.80 %
Moisture	..	..	..	0.24 %
Silicon, lead and bismuth oxide	..	..	..	traces only.
Total determined				.. 99.28 %



Electroscopic determination supported chemical estimation. Geological work by the Geological Survey of India and of Mysore, and electroscopic work by Yajnik and Kohli (Journal of the Asiatic Society of Bengal) have been referred to.

36. Magnetism and molecular structure, Part I: the magnetic susceptibilities of some inorganic sulphides and electronic isomers.

S. S. BHATNAGAR and S. L. BHATIA, Lahore.

In this paper the authors have determined the magnetic constants (at the room temperature) of the yellow and red sulphides of arsenic (solids) and also of their colloidal solutions in water. The determinations have been made with a modified Wilson's magnetic balance. The results show that Realgar ( $\text{As}_2\text{S}_2$ ) is less dia-magnetic than orpiment ( $\text{As}_2\text{S}_3$ ) both in the solid form as well as in colloidal solutions. These differences have been explained on the basis of atomic structure, and the valency theory of Langmuir. Work on other sulphides is discussed.

37. A note on isotopes:—

SATYENDRA RAY, Lucknow.

It is presumed from the "fine structure" of Thomson's parabolas that  $m$  for an atom is variable. Experimentally, however, all that we obtain is a change in the ratio  $e/m$  for an atom and the assumption that  $e$  is constant leads to the inference that  $m$  is variable.

Daecke in Phil. Mag. and Zeit. f. Phys. shows that statistically, the value of the electronic charge  $e$  is  $1/19$  ( $=1/20$  nearly) of the value given to us by Millikan. If we accept the possibility of the electronic charge being different from the value of Millikan, Aston's results may be taken to prove experimentally that the atom of electricity is, at least,  $1/10$  of that given by Daecke or  $1/200$  of that given by Millikan, rather than that the "atom of matter" possesses a variable mass.

38. Avogadro's number and "mean free path."

SATYENDRA RAY, Lucknow.

Millikan calls the mean free path a "hypothetical" quantity. It is shown that this mean free path is not related in any intimate manner with the properties of a gas like volume, pressure, temperature or

entropy, if the expression usually accepted for it, viz.  $\lambda = \frac{1}{\sqrt{2} \pi N \sigma^2}$

be correct. It is shown, instead, that the fairly close agreement of the Avogadro's number for different atoms means that the size of atoms

is very nearly identical and that perhaps  $\lambda = \left( 3 \sqrt{\frac{N}{3}} - \sigma \right)$  is a more

correct expression for the mean free path than the one usually accepted, which makes value of  $\lambda$  infinite when size of particle is infinitely small.

39. Fresh evidence in support of the chemical theory of fluorescence.

S. S. BHATNAGAR and KRISHNA GOPAL MATHUR, Lahore.

In support of the Perrin's view of the chemical nature of fluorescence, small changes in the refractive indices of eosin, fluorescein and acriflavin in their aqueous solutions have been observed on exposing



them to a concentrated beam of light from an arc lamp. The changes in the refractive indices when determined by means of the Rayleigh Interference Refractometer, by which a change in the refractive index of 1 in 100,000 could be ascertained with accuracy. Experiments were performed at various molecular concentrations, and the values obtained for the changes in the refractive indices were found to diminish at higher concentrations as the intensity of the fluorescent light decreased. Effect of the presence of gelatin and caustic soda has also been studied and in the presence of these substances the values for the changes were again observed to diminish, evidently on account of their retarding influence on the photo-decomposition of these fluorescent substances. Further work on the changes of other physical properties of the fluorescent substances on strong illumination and the influence of viscosity on their photo-decomposition is in progress.

#### 40. Vapour pressure of the soil.

RATTAN CHAND HOON, Lahore.

Experiments are described investigating method by which the relationship between the moisture content of a soil and its equilibrium vapour pressure may be determined by both a static and a dynamic method involving the use of the quartz spring micro-balance.

#### 41. Experiments on the hygroscopic-coefficients of thin films of colloidal matter.

MUKAND LAL, Lahore.

A method of measuring hygroscopic capacities of the colloidal fractions of soils is described when a microbalance in which Poyntings' double suspension mirror is employed.

Experiments, showing the influence of darkness, light and the various parts of the spectrum on the hygroscopic capacities of colloidal materials have been conducted with the object of testing results described by Linford 'Soil Science,' Vol. XXII.

#### 42. Reproducibility of hydrogen-calomel cells with low concentration of hydrochloric acid.

J. N. MUKHERJEE and K. KUMAR, Calcutta.

Abnormal values of e.m.f. are observed for such cells with dilute solutions of hydrochloric acid. According to Ellis (J.A.C.S., 38 (1916), p. 737) it is due to formation of basic chloride or sub-chloride and that the error is so large in solutions of HCl below 0.01 N "as to render measurements at these concentrations valueless." The present authors have observed that the process of equilibrium between a dilute solution of hydrochloric acid and calomel-mercury paste is very slow and that hydrochloric acid is adsorbed by the paste, causing a high value of e.m.f. of such cells.

#### 43. Evidence in favour of the existence of silver chromate in gelatine in the colloidal condition: electric conductivity of silver chromate in gelatine—II.

A. C. CHATTERJI and S. C. VARMA.

1. In a recent paper, Bolam and Mackenzie (Trans. Faraday Soc., 67, 160, 1926) have contested the conclusion of Chatterji and Dhar (Kolloid Z. 85, 2, 89, 1925) that Silver Chromate exists in the colloidal condition when precipitated in gelatine.



2. They re-affirm the conclusion of Williams and Mackenzie (J.C.S. 117, 844, 1925) that Silver Chromate exists in the ionic state in gelatine solution and does not behave as a protected colloid.

3. Experiments have been undertaken to determine accurately the electric conductivity of Silver Chromate of different strengths in gelatine of varying concentrations at 35°C., the silver chromate being produced by the addition of an equivalent quantity of silver nitrate and potassium chromate.

4. The results confirm the conclusions arrived at in previous papers (Proc. Ind. Science Congress, 1926; Trans. Faraday Soc., 72, 23, 1926). Moreover, the experimental evidences of Bolam and Mackenzie from the E.M.F. determinations have been thoroughly discussed and it has been pointed out from these results that except in a very few cases, not more than 40% of silver exist in the ionic condition. Or, in other words, a large percentage of silver exists in a form other than ionic, which supports our own conclusions, which have been arrived at from electric conductivity and diffusion experiments.

5. Experiments have also been undertaken to determine the electric conductivity of Lead Chromate in agar-agar solution and the results obtained have been discussed.

#### 44. Evidence in favour of the existence of silver chloride in gelatine in the colloidal condition : electric conductivity of silver chloride in gelatine—III.

A. C. CHATTERJI.

1. In previous papers (Proc. Ind. Science Congress, 1926, and Trans. Faraday Soc., 72, 23, 1926), it has been proved that silver chromate exists in the colloidal condition when formed in the presence of gelatine.

2. In this paper experiments have been undertaken to find out the electric conductivity of silver chloride of different strengths in gelatine of varying concentrations at 35°C., the silver chloride being produced by the addition of equivalent quantities of silver nitrate and potassium chloride.

3. Conductivity of equivalent concentration of silver nitrate and of potassium chloride in gelatine under identical conditions has also been determined for each set of experiment.

4. It has been found out from the above experiments that the conductivity of silver chloride is much less than what it should have been if it were in the ionic condition. In the majority of the cases investigated the conductivity of silver chloride and potassium nitrate produced along with it, is less than that of potassium nitrate alone, which means that potassium nitrate has been adsorbed by silver chloride in its course of formation, thereby lowering the active concentration of potassium nitrate.

#### 45. The heats of neutralisation of eugenol and isoeugenol.

G. GUNDU RAO.

A determination of the heats of neutralisation of these two isomers has been made, in order to study their acidic behaviour.

The heat of neutralisation of eugenol at about 25°C. when a slight excess of alkali is employed is found to be 6476 calories per mol. and 6790 calories per mol. with a large excess of alkali. Because of incomplete solution when an equivalent amount of alkali is employed and partial precipitation of the salt with a large excess the value for isoeugenol, 6550 calories per mol., is only approximate.

An attempt to determine the dissociation constants of the two compounds is being made.



46. The variation of extinction-coefficient with temperature.

B. K. MUKERJI and A. K. BHATTACHARJI.

It has been observed by us as well as by several other authors that in many photochemical reactions the yield per quantum changes markedly with temperature even when all other conditions are kept precisely constant. There is, however, no investigation on record proving that the amount of light absorption changes with temperature. The present investigation was taken up with a view to show that the extinction coefficients of some coloured solutions for the absorption of light in the visible region vary appreciably with changes in temperature—thus explaining the frequent increase in the quantum yield with temperature.

Fifteen coloured solutions were investigated and in all cases the extinction coefficients were found to increase systematically with increase in temperature.

In all cases straight lines are obtained when extinction coefficients are plotted against temperature.

The results have been explained from the point of view of the change of hydration of the solutes at higher temperatures.

47. The preparation and properties of triglycerides of fatty acids with an even number of carbon atoms.

R. B. JOGLEKAR and H. E. WATSON, Bangalore.

A number of triglycerides have been prepared by two different methods (1) heating the acid with glycerol in molecular proportions at reduced pressure at about 200°C (II) heating trichlorhydrin and the silver-salt of the acid in the presence of Xylol. The products obtained have identical properties after purification.

Values for the (1) Melting point, (2) Solidifying point (3) Density, (4) Viscosity, (5) Refractive index, (6) Surface tension as also the temperature coefficients in the last cases have been obtained for Stearin, Palmitin, Myristin, Laurin and Caprin. Their behaviour shows that in the liquid state they exist in one form only, and not as an equilibrium mixture of two forms.

The densities and viscosities of binary mixtures of stearin and palmitin have been determined at 8°. The curves obtained are almost straight lines.

48. Hydrolysis of gelatin.

B. N. DESAI and T. R. BOLAM.

The effect of hydrolysis of gelatin on its power to prevent the formation of  $\text{Ag}_2\text{CrO}_4$  from solutions of  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$  has been studied. It is found that the inhibitive power of gelatine first decrease, then increases and on further hydrolysis it again decreases.

The PH of the gelatine solutions (as measured by the colorimetric method) is increased to a small extent by hydrolysis and shows little variation with the progress of the latter.

It is also observed that by bringing the PH of hydrolysed gelatine to that of unhydrolysed by the addition of dilute acetic acid the inhibitive power of hydrolysed gelatine is in no way increased although the addition of the same amount of acetic acid to the unhydrolysed gelatine increases its inhibitive power a great deal.



## 49. Electro-motive behaviour of cupric oxide.

BASRUR SANJIVA RAO and N. G. CHOKANNA.

The half-cell platinum: cupric oxide, cuprous oxide, normal sodium hydroxide solution has been observed to give an inconstant potential difference by Allmand (J. C. S. 97,603,1910) and by Maddison (Trans. Far. Soc., p. 27, 1926) no satisfactory explanation being hitherto available.

The authors of this paper have carried out measurements with cells in which the cupric oxide used had been first warmed to dryness with an alcoholic solution of sodium hydroxide and then heated at different temperatures with suitable precautions. Such heating was found to cause an ageing effect which tends to give constant potential values.

No appreciable ageing effect was noticed with cuprous oxide under similar treatment.

## 50. The decomposition of nitrous oxide in the silent electric discharge: The kinetics of the reaction, Part II.

SHRIDHAR SARVOTTAM JOSHI.

In an investigation of the applicability of the law of the mass action in the case of the above reaction, it was found that the effect of varying the gas pressure on (1) the fractional change during a given time interval, and (2) the time corresponding to a constant fractional change, is in a sense opposite to that to be expected from the classical equations for the chemical reactions of the various 'orders.' A quantitative explanation of this result has been found in an analysis of the electrical factors (as a function of the gas pressure), which were found to be the chief determinants of the change. An exponential relationship has been found empirically between the gas pressure, and (1) the diminution of the percentage change in the initial stages and (2) the increase of the total time for the complete reaction, in several series of results. This relationship has been deduced on the basis of a theory advanced recently (Elliot, Joshi and Lunt, Trans. Farad. Soc., 1927, 23, 57). From this theory the critical energy for the first stage and for the complete decomposition of the nitrous oxide molecule in the discharge due to an electrionic collision has been calculated to a first approximation to be 0.9 volt and 3.0 volts respectively.

## 51. The decomposition of nitrous oxide in the silent electric discharge: the current and the energy variations during the reaction, Part III.

SHRIDHAR SARVOTTAM JOSHI.

During the course of a previous investigation on this subject (Joshi, Trans. Farad. Soc., 1927, 23, pp. 227-238) a remarkable variation of the discharge currents was observed relating to the different stages of the above reaction. It appeared from the literature that no instance of this phenomenon has been observed; it has therefore been investigated in some detail. The value of the current in the ionisation space, and the corresponding rate of change diminish from large initial values during the first phase, become very small in the intermediate stage, and show a sudden increase towards the end of the decomposition. The duration of any given phase, the actual value of each of the quantities mentioned above, and its rate of change with time vary systematically with respect to the initial pressure for a constant applied potential. These results have been traced to the corresponding variation in the intensity of the ionisation, and of the mean electrionic velocity, due to the presence of nitrogen peroxide, which appears as an intermediate product of the



decomposition of nitrous oxide in the discharge. A mechanism of the complete reaction has been advanced from the data for the composition of the gaseous mixtures at successive times during the decompositions, started at different initial pressures.

52. The decomposition of nitrous oxide in the silent electric discharge: further investigations on the current and the energy variations during the reaction, Part IV.

SHRIDHAR SARVOTTAM JOSHI.

A confirmation of the explanation advanced in Part III of this series for the marked and the concomitant variation of the significant electrical quantities and of the reaction rate has been observed in a study of the dielectric strength, of the reaction mixture during the course of the decomposition. A study has also been made of the dielectric strength of nitrous oxide as a function of the gas pressure in different frequencies of the A. C. supply.

53. The decomposition of nitrous oxide in the silent electric discharge, Part V.

SHRIDHAR SARVOTTAM JOSHI.

The admixture of foreign gases mentioned below with a constant amount of nitrous oxide diminishes, (1) the percentage change in a given time, (2) the discharge current, (3) the energy consumed in the reaction vessel, and (4) the inverse of the dielectric strength of the gas. The effect increases by increasing the amount of the contaminant, the order being  $N_2 > \text{air} > O_2 > NO_2$ . Further the inhibition of the decomposition due to addition of  $N_2$  and  $O_2$  applied respectively only to the first stage of the reaction and to the complete reaction, as judged from the marked difference. The characteristic values of the ratio  $N_2/O_2$  for the decomposition mixture in the two cases (cf. Part I, loc. cit.). Diminution of the frequency of the A. C. supply reduced the percentage change except at very small frequencies.

54. Interaction of epichlorhydrin and cyclohexene oxide with alkali and ammonium halides.

HEMENDRA KUMAR SEN, CHITTARANJAN BARAT *and*  
PATIT PABAN PAL. Calcutta.

When these oxides act upon alkali and ammonium halides a very interesting reaction takes place with the liberation of alkali hydroxides and ammonia. In fact this can be shown as a lecture experiment. With an excess of ammonium chloride, the velocity of reaction of epichlorhydrin and cyclohexene oxide has been determined:

Epichlorhydrin: ammonium chloride :: 1 mol : 10 mols. (0.925 gram epichlorhydrin, 5.35 gram of pure ammonium chloride and 20 c.c. of pure absolute alcohol were made up to 250 c.c. with distilled water and placed in a thermostat at 35°C. At an interval of 1 hour, 10 c.c. of the solution was taken out, at once mixed with an excess of cold water and titrated with N/100 sulphuric acid).



Time in hrs.	C. cs. of N/100 $H_2SO_4$ used.		Mean titre.	Velocity constant $K = \frac{1}{t} \ln \frac{a}{a-x}$
	Expt. I.	Expt. II.		
1 hour ..	2.765	3.065	2.915	0.2040
2 hours ..	4.877	4.904	4.890	0.1851
3 „ ..	6.938	7.100	7.019	0.1960
4 „ ..	8.848	8.787	8.817	0.2042
5 „ ..	10.709	9.502	10.105	0.2040
.....	.....	.....	.....	.....
24 „ ..	15.86	15.734	15.797	.....

Time in hrs.	C. cs. of $N/100$ $H_2SO_4$ used.		Mean titre.	Velocity constant $K = \frac{1}{t} \ln \frac{a}{a-x}$
	Expt. I.	Expt. II.		
Epichlorhydrin : Ammonium. Chloride : 1 : 50.				
1 hour ..	13.13	13.1	13.12	0.5625
2 hours ..	20.8	20.74	20.77	0.5715
3 „ ..	24.8	24.75	24.78	0.5584
4 „ ..	27.57	27.57	27.57	0.5865
5 „ ..	29.39	29.48	29.44	0.6734
6 „ ..	30.49	30.48	30.49	....
.....	.....	.....	.....	.....
24 „ ..	30.49	30.48	30.49	....

With epichlorhydrin : ammonium chloride :: 1 : 100,  $K=0.9523$ , when the volume of solution is made up as described before, i. e. made up to 250 c. c. If, however, the volume is doubled retaining the same molecular proportion between the reactants,  $K=0.4437$ ; when the volume is quadrupled,  $K=0.2442$ .

### 55. Reactions at the surface of hot metallic filaments— Platinum, Platinum-Iridium alloys and Tungsten.

B. S. SRIKANTAN.

The nature and course of the reaction  $H_2 + Co_2 \rightarrow Co + H_2O$  have been studied at the surface of platinum, platinum-iridium alloys (composition :— 5, 10, 15, 20, 25 and 30 per cent. iridium) and tungsten at temperatures between  $1000^\circ$  and  $1600^\circ$  C. The reaction is unimolecular in all cases. The alloys are more active than pure platinum. The alloys of composition 20, 25 and 30 per cent, iridium change their activity with use while those of 5, 10 and 15 per cent. are steady. Tungsten is more active than platinum but less so than platinum-iridium alloys. The temperature-coefficient and the apparent heats of activation have been calculated in each case from the observed velocity constants. Microscopic examination of the filaments before and after the reaction shows that the nature of the surface is greatly altered.



## 56. Esterification in the gaseous phase with solid catalysts.

N. G. GAJENDRAGAD.

The esterification of methyl and ethyl alcohols with acetic acid has been studied using potassium alum and silica catalysts at 230°C. The equilibrium constant has been found to be not far from that obtained by other observers in the liquid phase at lower temperatures.

## 57. Studies on the substituted quaternary azonium iodides, Part V. The molecular state of phenyldimethyl azonium, phenylmethylethyl azonium, phenyldiethyl azonium, phenylmethylbenzyl azonium, phenylpropylbenzyl azonium iodides in solution.

BAWA KARTAR SINGH *and* MOLA RAM SUD.

The molecular weights of five substituted quaternary azonium iodides are determined, using the Lumsden-Walker boiling-point method, in water and ethyl alcohol. The solutions employed are very dilute, the concentration, in most cases, ranging from 0.6 to 1.5 per cent. The following conclusions are drawn from this work:—

1. The molecular weights of phenyldimethyl azonium, phenylmethylethyl azonium, phenylmethylbenzyl azonium and phenylpropylbenzyl azonium iodides are lower in ethyl alcohol than in water; in the case of phenyldiethyl azonium iodide this relation is reversed. The degree of dissociation is, therefore, greater in ethyl alcohol, a solvent of low dielectric constant, than in water, a solvent which has a very high value. It is, therefore, clear that the Nernst-Thomson rule is not followed in these cases.

2. In aqueous solution, the degree of dissociation of the above mentioned substituted quaternary azonium iodides increases with increasing formula-weight of the base; but this regularity does not appear in ethyl alcohol.

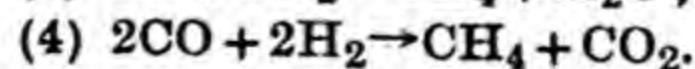
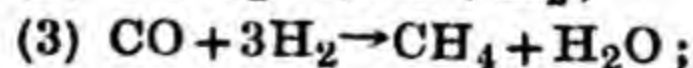
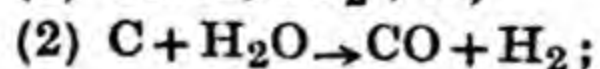
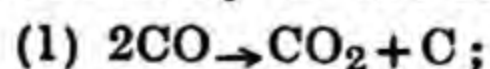
3. The degree of dissociation of the salts increases with dilution in both the solvents.

4. The molecular weights furnished by the two methods, namely, the volume and the weight methods, are nearly identical for very dilute solutions.

## 58. Catalytic preparation of a gas rich in methane from a mixture of watergas and steam.

J. C. GHOSH *and* K. CHAKRAVARTY, Dacca.

In previous investigations, the authors have shown that a gas mixture containing CO and H<sub>2</sub> in 1:1 by volume can be made to yield a fuel gas containing over 25% methane if passed over suitable catalysts at temperatures 350°—450°C. The efficiency and life of certain catalysts have now been very considerably increased by introducing steam in suitable proportions in the reacting gas mixture. The following reaction takes place simultaneously on the catalyst surface:—



It will be seen from (1) and (2) that carbon monoxide reacts with steam giving carbon dioxide and hydrogen. The hydrogen so produced increases the ratio of H<sub>2</sub> to CO in the reacting gases, and prolongs the life of the catalyst by preventing deposition of carbon. Catalysts have



been found which also regulate the rates of the reactions given above, that the resulting fuel gases after removal of  $\text{CO}_2$ , contain more than 50%  $\text{CH}_4$ .

### 59. The constitution of Bixin—Part I.

R. ROBINSON and K. VENKATARAMAN.

Using ethyl acetate as solvent the catalytic reduction of bixin to octadecahydrobixin (Herzig and Faltis, 1923) has been confirmed. But in glacial acetic acid solution, only 14 atoms of hydrogen were absorbed. The resulting oil was esterified and this hydrogenated bixin methyl ester was found to take up approximately 4 atoms of bromine.

Oxidising octadecahydrobixin ( $\text{C}_{25}\text{H}_{48}\text{O}_4$ ) in glacial acetic acid with chromic acid corresponding to 6, 9 and 12 atoms of oxygen respectively, the product in each case—a mobile liquid completely soluble in sodium carbonate solution—was analysed. In the last instance the product had b.p.  $210\text{--}230^\circ\text{C}$ . 2–4 mm. The analysis corresponded closely to  $\text{C}_{25}\text{H}_{48}\text{O}_5$ .

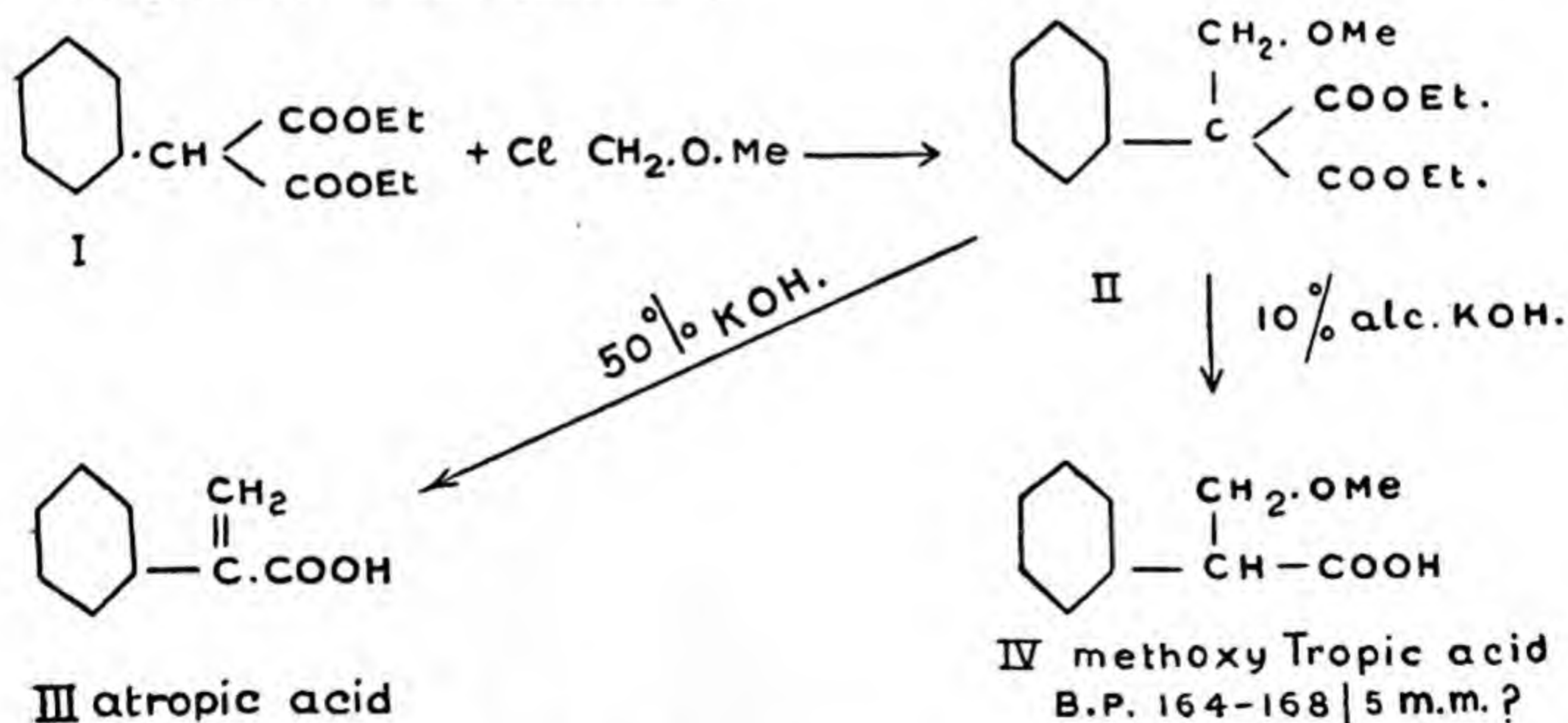
Oxidising bixin itself similarly, two crystalline substances—(1) needles, m.p.  $130\text{--}140^\circ\text{C}$ . and (2) prisms, decomposing above  $200^\circ\text{C}$ . have been obtained, but neither has yet been characterised.

Bixin is known to be the monomethyl ester of a dicarboxylic acid. Neither from methyl bixin nor from hydromethyl bixin could a definite hydrazide be prepared. With methyl bixin the result was a small yield of microscopic crystals decomposing above  $250^\circ\text{C}$ .

### 60. Condensation of mono-chlor methyl ether with phenyl malonic ester.

M. GOPALA RAO and J. L. SIMONSEN.

This paper is in continuation of the Monochloro methyl ether condensations carried out by Dr. J. L. Simonsen and embodies the results so far obtained in the above. This describes a simple method of synthesising atropic acid. Work is proceeding.

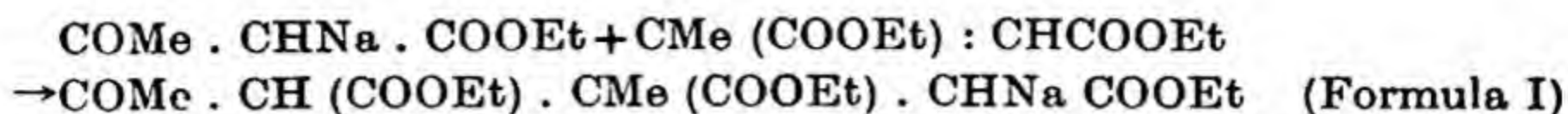


### 61. Studies in Michael condensation.

PRAFULLA CHANDRA MITTER and ASOKE CHANDRA RAY,  
Calcutta.

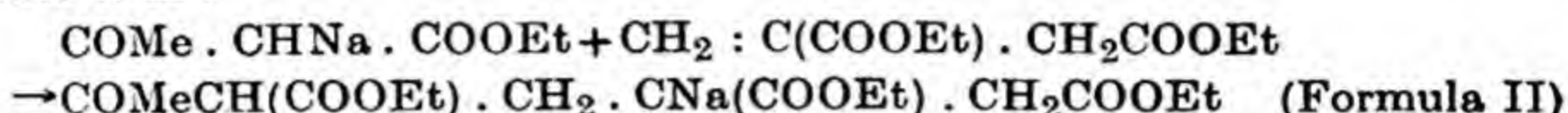
By the condensation of ethyl-sod-acetoacetate with ethyl citraconate in alcoholic solution, Michael (J. pr. Chem 1887 (2) 35 351) obtained an additive product  $\text{C}_{15}\text{H}_{24}\text{O}_7$  and interpreted the reaction as follows:—





An acidic product was formed at the same time which M. could not purify and left unstudied.

On repeating M's experiment under different conditions we found that the reaction had followed a different course in the case actually studied by M. The citraconic ester had under the influence of alcoholic sodium hydroxide undergone transformation into Itaconic ester (c.f. Hope T. 1912, 101, 892), which had condensed with ethyl sod-aceto-acetate thus:—



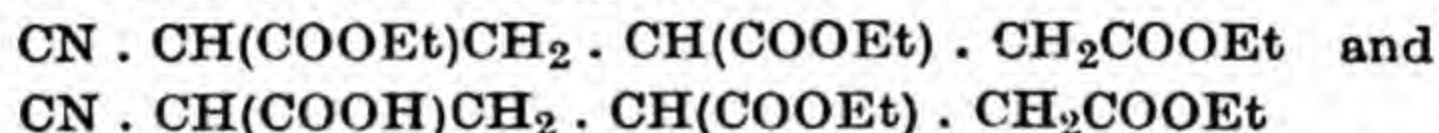
This was confirmed by condensing itaconic ester with acetoacetic ester in presence of "molecular" sodium in ether when an identical product was formed. A substance having formula (I) is formed when the condensation between the two reactants takes place in presence of "dry" sodium ethoxide or molecular sodium.

The products of acidic nature which always accompany these condensation products could not be isolated in the pure state but analysis of their semicarbazones show that they are di-hydroresorcinol derivatives.

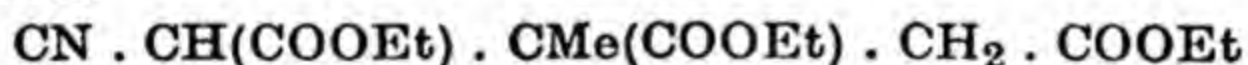
Similar results were obtained with ethyl citraconate and ethyl-methyl-aceto-acetate.

In the case of condensation of fumaric ester with ethyl aceto-acetate (first studied by Ruhemann and Browning (T. 1898, 73 282) or with ethyl-methyl aceto acetate there is no possibility of isomeric change and the same condensation products are obtained whether the condensing agent is sodium ethoxide in alcohol or "molecular" sodium in ether. Here also we could isolate the semicarbazones of the ring-compounds.

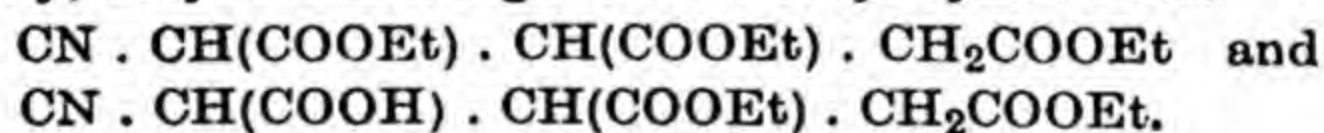
Condensation of ethyl citraconate with ethyl cyanacetate gave in presence of alcoholic sodium ethoxide



(Vide Perkin and Thorpe T. 1899, 75, 52). With "molecular" sodium we obtained



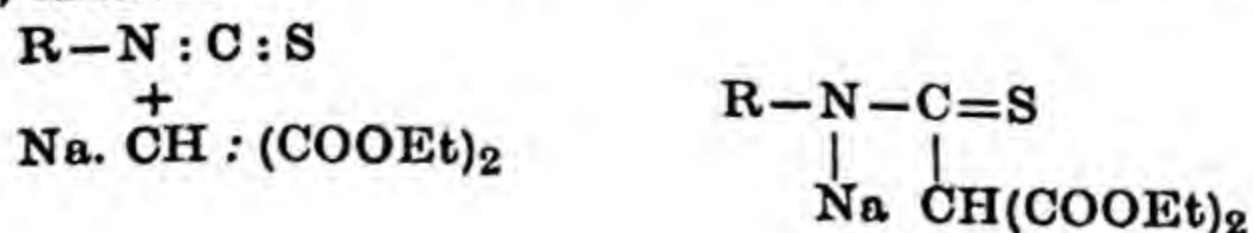
Lastly, ethyl fumarate gave with ethyl cyanacetate



## 62. Extension of Michael's reaction.

P. C. GUHA and M. N. CHAKLADAR.

Michael's reaction takes place between sodium derivatives of aceto-acetic ester, malonic ester and cyanacetic ester and compounds of the general formula  $\text{RCH} : \text{CHX}$  or  $\text{RC} : \text{CX}$  in which R is a positive or negative organic radical and X is a strongly negative radical like carboxyl or cyanogen. The action of the above mentioned sodium derivatives has now been studied upon mustard oils and isocyanates and the double bond existing between the nitrogen and carbon atoms opens up the possibility for the sodium atom and the rest of the molecules  $[-\text{CH}(\text{COOEt})_2, \text{CH}_3 \cdot \text{CO} \cdot \text{CH} \cdot \text{COOEt}]$  and  $\text{CN} \cdot \text{CH} \cdot \text{COOEt}$  to be attached to both of its sides, thus:—





which gets easily decomposed by acids, to yield compounds of the general formula  $\text{RNH-CS-CH}_3$  together with carbon dioxide and alcohol. Isocyanates react similarly to yield compounds of the general formula  $\text{RNH-CO-CH}_3$ .

### 63. Replacement of sulphonic groups by nitro-groups in aromatic halogen compounds.

P. S. VARMA and K. A. JOSHI.

It has been shown (Datta and Varma, Jour. Am. Chem. Soc. 1919, 41, 2039; Jour. In. Chem. Soc. 19127) that sulphonic groups can easily be replaced by nitro groups in aromatic phenolic and amino-compounds by means of nitrous gases. This investigation has been continued further and it has been possible to replace the sulphonic groups by nitro groups in a number of halogen derivatives of aromatic hydro-carbons.

### 64. Influence of substitution on the oxidation of side-chain in the benzene nucleus.

P. S. VARMA and P. B. PANICKER.

The authors have used a neutral solution of potassium permanganate as an oxidising agent and have oxidised p-nitro-toluene, p-toluic acid, p-chloro-toluene, p-bromo-toluene, p-iodo-toluene, p-aceto-toluidine, p-methyl cresyl ether, m-toluic acid, m-nitro-toluene, m-aceto-toluidine, m-methyl cresyl ether, o-toluic acid, o-nitro-toluene, o-chloro-toluene, o-bromo-toluene, o-iodo-toluene and o-aceto-toluidine under the identical experimental conditions and have come to the conclusion that in the p-series the order (the degree of oxidation decreasing) in which the side-chain is oxidised is  $\text{-COOH}$ ,  $\text{-NO}_2$ ,  $\text{-Br}$ ,  $\text{-Cl}$ ,  $\text{-OCH}_3$ ,  $\text{-I}$ ,  $\text{-NHCOCH}_3$ , and in the o-series the order is  $\text{-NO}_2$ ,  $\text{-COOH}$ ,  $\text{-Br}$ ,  $\text{-Cl}$ ,  $\text{-NHCOCH}_3$ , and  $\text{-I}$ . Regarding position isomers, there does not seem to be any regularity. p-Nitro-toluene is oxidised most, the m-body the least whereas in the aceto-toluidines, o-derivative comes first and the p-derivative last.

### 65. Nitration of benzene.

P. S. VARMA and K. A. JOSHI.

Benzene has been nitrated by means of nitric acid alone in presence of zinc, copper, tin, and antimony as catalysts. It has been possible to get some increase in the yield of nitro-benzene in presence of metallic tin, but the yield so obtained can in no way be compared with the yield obtained by using a mixture of nitric and sulphuric acid as is done in the ordinary nitration.

### 66. Studies in the anthracene series. Halogenation and nitration (Preliminary).

P. S. VARMA and A. SUBRAMANYAM.

Mono-iodo and di-iodo-anthraquinone (the latter for the first time) have been obtained by the action of sodium nitrite and fuming sulphuric acid on anthracene and iodine. A number of bromo-compounds have also been obtained by the action of bromine and fuming sulphuric acid. Some of these halogenated compounds have also been nitrated. In some cases nitro-derivatives have been obtained whilst in others the halogen compounds are decomposed and the halogens liberated.



67. Nitration by means of a mixture of nitro-sulphonic and fuming nitric acids. Part II.

P. S. VARMA and S. K. SHARMA.

This is in continuation of the work by Varma and Kulkarni (Jour. Am. Chem. Soc. 1925, 47, 143.) Sulphanilic acid,  $\alpha$ -nitro-naphthalene, o-amino-benzoic acid, m-amino-benzoic acid, p-amino-benzoic acid, amino-aceto-phenone, naphthylamine-sulphonic acids have been tried and a number of nitrated products obtained from them.

68. The influence of water and sulphuric acid in the nitration of hydrocarbons, Part I.

D. D. KARVE and A. B. KUMTHEKAR.

The investigation has been undertaken with a view to find out which

of the two forms of nitric acid, the pseudo form  $\begin{array}{c} \text{O} \\ \parallel \\ \text{O} = \text{N} - \text{OH} \end{array}$  or the aci-

form  $\text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \text{H}$  or the dissociated acid  $\text{H}^+ + \left\{ \text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \right\}^-$  was

responsible for the nitration of hydrocarbons.

The work of Schäfer and of Hantzsch has shown that nitric acid has absorption spectra either resembling its salts or resembling its esters depending upon the solvent and also upon the concentration.

Nitration of benzene, toluene, the xylenes as also of some heterocyclic compounds was undertaken, using definite quantities of the substances with varying quantities of nitric acid in different dilutions and also of varying proportions of nitric acid and sulphuric acid and the extent of nitration estimated by means of the estimation of the  $\text{NO}_2$  group.

On account of the mutual solubility of nitric acid and the nitro-compound, the measurement of the yield of the compound was rendered rather difficult and special methods of procedure had to be employed. (cf. Spindler Ann. 224).

The results obtained up to now seem to indicate that the acid with the formula seems to be responsible for the nitrations. The work is still in progress.

69. Dyes derived from oxalyldibenzylketone.

S. A. SALETORÉ and GOPAL CHANDRA CHAKRAVARTI.

Several investigators have so far found that the hydroxyiminazoles obtained by condensing phenanthraquinone and acenaphthaquinone with salicylaldehyde in presence of ammonia are all colourless crystalline compounds (Japp. and Streatfield. J. C. S. 1882, 41, 146. and others), but those derived from substituted salicylaldehydes are coloured (Sircar and Sircar. J. C. S. 1923, 123, 1559.) It was therefore anticipated that the iminazole from oxalyldibenzylketone and salicylaldehyde would likewise be colourless; whereas this compound was obtained as a deep brown coloured crystalline product with marked chromophoric properties. This is evidence in support of the observation made by one of us recently (Chakravarti J. I. C. S. 1925, 2, 71) that oxalyldibenzylketone is a much better chromophore than phenanthraquinone or acenaphthaquinone



although the latter bodies contain condensed benzene nuclei. Several other iminazoles derived from oxalyldibenzylketone on the one hand and vanillin, nitrosalicylaldehyde, *p*- and *m*-hydroxybenzaldehydes, resorcyaldehyde, bromosalicylaldehyde, etc., on the other, are also found to be deeply coloured.

#### 70. Diazotisation of difficultly diazotisable amines.

S. KRISHNA and RATAN LAL BHATIA.

The usual methods of diazotisation are not workable in the case of certain substituted amines; nor are such treatments as pressure, high temperature, concentration, solvents, etc., applicable in all cases. Realising this difficulty, a method has been worked out in which the use of a basic solvent like pyridine has been made. The procedure employed is to make a solution of the desired amine in minimum quantity of pyridine and adding to it a strong solution of sodium nitrite (calc. quantity) in water. This mixture is then added to a dilute solution of HCl very slowly in small quantities, when it is found that diazotisation proceeds satisfactorily. In this way tribromaniline, 2 : 6 dichloro-*p*-nitraniline, dibromo-*p*-aminobenzoic acid and dibromo-*p*-aminobenzaldehyde have been successfully diazotised.

#### 71. Synthesis of straight chain unsaturated acids

R. BHATTACHARYA and J. L. SIMONSEN.

It has been recently suggested that iso-erucic acid is an inseparable mixture of two unsaturated acids which may be synthesised from (a) octinine and 14-iodo tetradecan acid, and (b) undecinin and 10-bromoundecylic acid. As a preliminary to their preparation the synthesis of homologous acids has been tried. 12-iodo-dodecan acid has been prepared, in the following way, and condensed with the sodium compound of decinin to get behenolic acid.

Castor oil → Undecylenic acid → 10-Bromoundecylic Me-ester → cyano undecylic Me-ester → decamethylene dicarboxylic Me-ester

Potassium salt of the half hydrolysed ester → 12-hydroxy Lauric acid → 12 Iodo-Lauric acid.

Decinin was prepared by the action of mono sodium acetylde on octyl iodide.

#### 72. Synthetical experiments in the flavone series—Part I a synthesis of 7 : 8-dihydroxy-2-methylchromone and of 7 : 8-dihydroxyflavone.

K. VENKATARAMAN.

The method of Allan and Robinson for the synthesis of flavonols is now being extended to the preparation of flavones and flavonols containing hydroxyls in 7 : 8-positions. Thus, by the condensation of gallacetophenone with acetic anhydride and sodium acetate and hydrolysis of the product, 7 : 8-dihydroxy-2-methylchromone has been prepared; and 7 : 8-dihydroxyflavone by the interaction of gallacetophenone, benzoic anhydride and sodium benzoate. The reactions and dyeing properties of these substances are described.

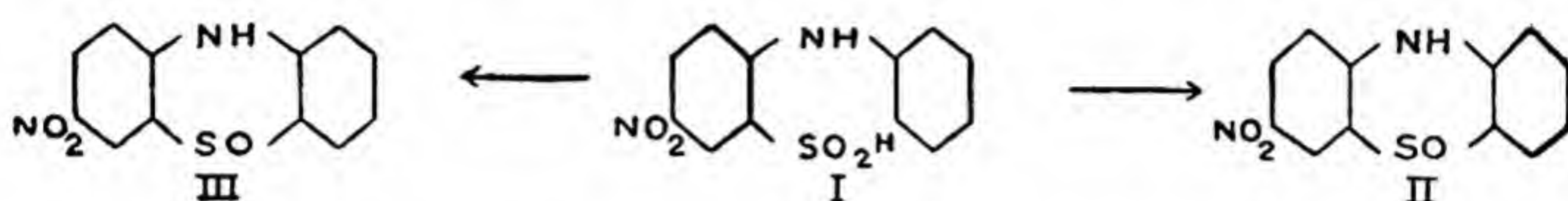
The synthesis of other hydroxyflavones derived from gallacetophenone and *ω*-methoxygallacetophenone is in progress. The latter compound, to which no reference is found in the literature, is being prepared by the action of methoxyacetic acid on pyrogallol in presence of zinc chloride.



## 73. Synthesis of substituted thiazines.

S. KRISHNA and MITTER SAIN JAIN.

Literature on substituted thiazines shows that the methods of preparation hitherto described give only the symmetrically disubstituted derivatives and are applicable only in a very limited number of cases. An attempt is now being made to synthesise mono, di-or polysubstituted thiazines by a method that should be applicable to benzene derivatives containing acid or basic substituents. The present communication describes the synthesis of thiazine by a method which utilises the reactivity of the halogen atom in negatively substituted chlorobenzene. 6, chloro—3—nitrobenzene sulphinic acid condenses with anilines, 4 nitro—2 sulphino-diphenylamine (I) being formed.



This is readily soluble in sulphuric acid. If the blue solution obtained is immediately diluted with water, the sulphoxide (II) will be precipitated, but if the solution is kept for half an hour before dilution, 3—nitrothiazine (III) will be obtained and sulphur dioxide evolved.

3—nitrothiazine is readily reduced to 3—aminothiazine from which through the diazo-compound thiazine is obtained.

A blue colour is produced when a solution of 3—nitrothiazine in acetic acid is treated with hydrogen chloride. The production of this blue colour has been regarded as evidence of the existence of quinonoid dithionium salts. Attempts have been made to isolate such salts but these have not been successful due probably to the influence of a nitro group.

The present work is interesting because the starting material contains a nitro-group, the presence of which in the molecule has been found to inhibit the course of other methods of synthesis.

## 74. A new synthesis of morin and a note on the constitution of lotoflavin.

R. ROBINSON and K. VENKATARAMAN.

The condensation of  $\omega$ -methoxyphloracetophenone with dimethyl- $\beta$ -resorcylic anhydride and sodium dimethyl- $\beta$ -resorcyate and hydrolysis of the product gave 5 : 7-dihydroxy-3 : 2' : 4'-trimethoxyflavone in good yield. Demethylation of this yielded 3 : 5 : 7 : 2' : 4'-pentahydroxyflavone identical with naturally occurring morin.

Hydrolysis of the product of the interaction between phloracetophenone, dimethyl- $\beta$ -resorcylic anhydride and sodium dimethyl- $\beta$ -resorcyate yielded 5 : 7-dihydroxy-2' : 4'-dimethoxyflavone. Demethylation led to 5 : 7 : 2' : 4'-tetrahydroxyflavone—the constitution ascribed to "lotoflavin," the coloring matter of *Lotus arabicus*, by Dunstan and Henry. The properties of the synthetic tetrahydroxyflavone and direct comparison of it with Dunstan and Henry's "lotoflavin" showed that the two substances were entirely different. From an examination of "lotoflavin" it appears probable that "lotoflavin" is a mixture of two flavones, one of which at least has a hydroxyl in the 3-position.



## 75. On the constitution of some dinitro-m-Cresols.

S. M. SANE and S. S. JOSHI, Lucknow.

There are contradictory statements regarding the constitutions of dinitro-m-cresols. Gibbs and Robertson have described two dinitro-m-cresols: (1) 1-methyl 3-hydroxy-2 : 6-dinitrobenzene (m.p. 74°C) and (2) 1-methyl 3-hydroxy 4 : 6-dinitrobenzene (m.p. 60°C). Will prepared from one of the trinitrotoluenes 1-methyl 3-hydroxy 4 : 6-dinitrobenzene (m.p. 74°C), while Borsche prepared 1-methyl 3-hydroxy 4 : 6-dinitrobenzene (m.p. 63-65°C) from 3-chloro 4 : 6-dinitrotoluene. According to these statements there are thus two dinitro-m-cresols which have the same constitution but different melting points and two dinitrocresols having different constitutions have the same melting points.

Investigation has shown that Borsche's 1-methyl 3-hydroxy 4 : 6-dinitrobenzene has the m.p. 74°C. Its constitution has been further confirmed by the fact that this dinitro-m-cresol and 3-chloro 4 : 6-dinitrotoluene from which it is prepared, yield the same dinitrotoluidine. Gibb's and Robertson's dinitro-m-cresol of m.p. 74°C is therefore 1-methyl 3-hydroxy 4 : 6-dinitrobenzene and the bromo derivative which they and Kehrmann prepare has the constitution 1-methyl 2-Bromo 3-hydroxy 4 : 6-dinitrobenzene. The 1-methyl 2-bromo 3-chloro 4 : 6-dinitrobenzene prepared from the last compound is identical with the chlorobromodinitrotoluene prepared by Cohen and Smithells.

## 76. Camphor as a preservative for tan-liquors.

P. D. DALVI.

*Aspergillus niger* and certain other fungi are constantly found in tan liquors and bring about a reduction in the tanning value of the liquors owing to the fermentation of the tannic acid induced by the organism. The action of various disinfectants or preservatives in diminishing this loss has been investigated and of these tried camphor seems the most promising, being efficient in small quantities and without harmful effect on the activity of the liquor.

## 77. Lengthened ortho-di-derivatives of benzene and their ring-closure : Part I.

P. C. GUHA and T. N. GHOSH.

Ortho-nitrophenyl-4-arylthiosemicarbazides on reduction with tin and hydrochloric acid yield simultaneously (a) 1-o-aminophenyl-4-arylthiosemicarbazides  $C_6H_4(NH_2) \cdot NH \cdot NH \cdot CS \cdot NHR$  and (b) 1-N-R-2 : 3-benzo-6-thiol-1 : 4 : 5-triazines. Compounds of type (a) can be converted into compounds of type (b) on treatment with acetic anhydride and strong hydrochloric acid showing conclusively that in the reduction process the formation of (a) precedes that of (b). The reactive amino-group of compounds of type (a) has been utilised by allowing it to react with carbimides and thiocarbimides, potassium cyanate and thiocyanate and aldehydes when the following types of lengthened ortho-di-derivatives of benzene (viz.  $R'NHCO \cdot NH \cdot C_6H_4 \cdot NH \cdot NH \cdot CS \cdot NHPh$ ,  $R'NH \cdot CS \cdot NH \cdot C_6H_4 \cdot NH \cdot NH \cdot CS \cdot NHPh$  and  $RCH : N-C_6H_4-NH \cdot NH \cdot CS \cdot NHPh$  where  $R_0-Ph$ , tolyl, xylyl, allyl, or H) are obtained and they have been made to yield various types of ring-closed compounds, viz. benzo-thio-octa-triazines and benzo-octa-tetrazines. Compounds of type (a) give benzo-thio-hepta-triazines and benzo-hepta-tetrazines respectively on treatment with ferric chloride and hydrazine hydrate.



## 78. Lengthened ortho-di-derivatives of benzene and their ring-closure : Part II.

P. C. GUHA and T. N. GHOSH.

Ortho-nitrophenylsemicarbazides on reduction, yield simultaneously (a) ortho-amino-phenyl-semicarbazides and (b) benzo-triazines. Compounds of type (a), by virtue of the amino group present in it, react with carbimides, thiocarbimides, aldehydes, ferric chloride, hydrazine hydrate, etc., to yield 1-carbamido-2-semicarbazido-o-benzene, 1-thiocarbamido-2-semicarbazido-benzene, 1-o-benzal-anilino-semicarbazides, 3:4-benzo-7-R-amino-1:2:5:6-oxheptatriazines and 1-N-R-3:4-benzo-7-hydroxy-1:2:5:6-hepta-tetrazines. The nitro-hydrazine reacts with potassium cyanate, potassium thiocyanate, o-chlorbenzaldehyde, glyoxal, CS<sub>2</sub>, KOH, MeI, COCl<sub>2</sub>, Cl, COOEt to yield o-nitrophenyl-semi-carbazide, o-nitrophenyl-thiosemicarbazide, chlorbenzaldehyde-o-nitrophenylhydrazone, glyoxal-o-nitrophenyl-osazone, o-nitrophenyl-methyl-dithiocarbazine, di-o-nitrophenyl-carbohydrazide and o-nitrophenyl-ethyl-carbazinate and they have been found to form 5 or 6 or 7 or 8 or 10-membered heterocyclic compounds, as the case may be on reduction.

## 79. Hetero-ring formations with 1-substituted thiocarbohydrazides : Part I.

P. C. GUHA and S. K. RAY CHOUDHURY.

Due to the presence of two hydrazine groupings, thiocarbohydrazide reacts with various organic substances: (Guha and De, Soc., 1924, 125, 1215; J. Indian C. S., 1924, 1, 141; 1925, 2, 225). It was expected that if one of these two hydrazino groups be substituted the behaviour of the resulting carbohydrazides would be different from that of the unsubstituted product. With this object in view a number of mono-aryl-substituted-thiocarbohydrazides (of which not a single member is known up to this time) have been prepared by the action of hydrazine hydrate upon aryl-dithiocarbazinates and they have been found to form oxdiazines with ortho-diketones, oxheptatriazines with monoximes of 1:2-diketones, pyrazoline derivatives with ketonic esters, thio-octa-diazines with 1:4-diketones, thiodiazines with halogenated ketones and esters. The aldehyde-aryl-thiocarbohydrazones give 2-phenylhydrazino-5-R-1:3:4-thiodiazoles by the oxidising action of ferric chloride and 2-aldehydehydrazones of 2:5-diketo-4-aryl-tetrahydro-1:3:4-thiodiazines with halogenated ketones and esters.

## 80. Hetero-ring formations with substituted thiocarbohydrazides : Part II.

P. C. GUHA and S. K. RAY CHOUDHURY.

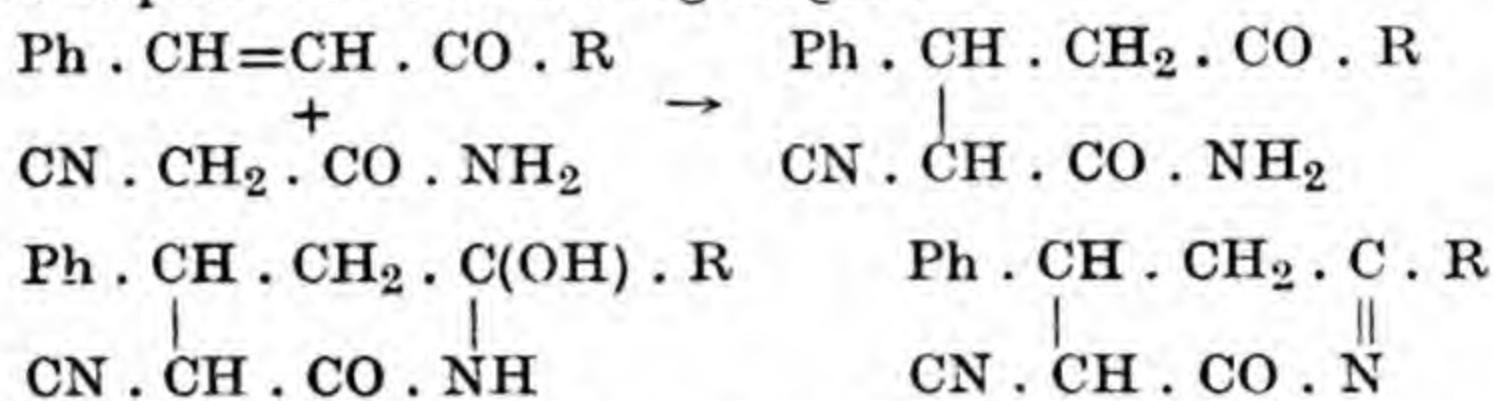
In this part, the action of formic acid, acid chlorides and anhydrides, carbimides and thiocarbimides have been studied. 2-Anilinomino-1:3:4-thiodiazole and 2-anilinamino-5-thiol-1:3:4-thiodiazole are obtained from formic acid and potassium ethyl xanthate; thionyl, malonyl and phthalyl chlorides yield 2-anilinamino-5-oxy-5:1:3:4-dithiodiazole, 2-anilinamino-5:7-diketo-1:3:4-thioheptadiazine and 2-anilinamino-5:8-diketo-6:7-benzo-1:3:4-thio-octadiazine respectively. The action of chlorides of dibasic acids upon aldehyde-aryl-thiocarbohydrazones and the action of different ring-closing agents (e.g. HCl, NaOH, FeCl<sub>3</sub>, etc.) upon the mustard oil and isocyanate derivatives have been found to yield different types of thiobiazole and triazole derivatives.



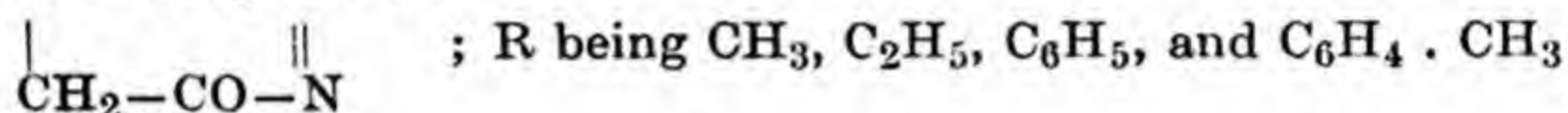
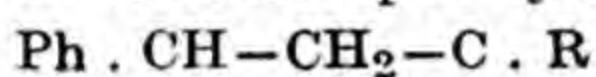
# 81. Study in the condensation of compounds with conjugated double bonds with reactive methylene groups.

CHITTARANJAN BARAT, Calcutta.

The condensation between compounds like Benzalacetone, with one like Cyanoacetamide, was first observed by Sen (J.C.S., Trans., 107, 1366) who, did not, however, study the mechanism of the reaction. The present work was undertaken with a view to do that, as well as to compare the effects of different condensing agents, e.g. Sodium Ethoxide (Michael), Piperidine (Knoevenagel), Ammonia, etc. Cyanoacetamide has been made to condense with (1) Benzalacetone, (2)  $\alpha$ -Benzalmethylethyl ketone, (3) Benzalacetophenone, and (4) Benzal-*p*-Methylacetophenone, under all the different conditions mentioned above. The reactions appear to take place in the following stages:—



all of which upon hydrolysis finally yield the Pyridine derivative:—



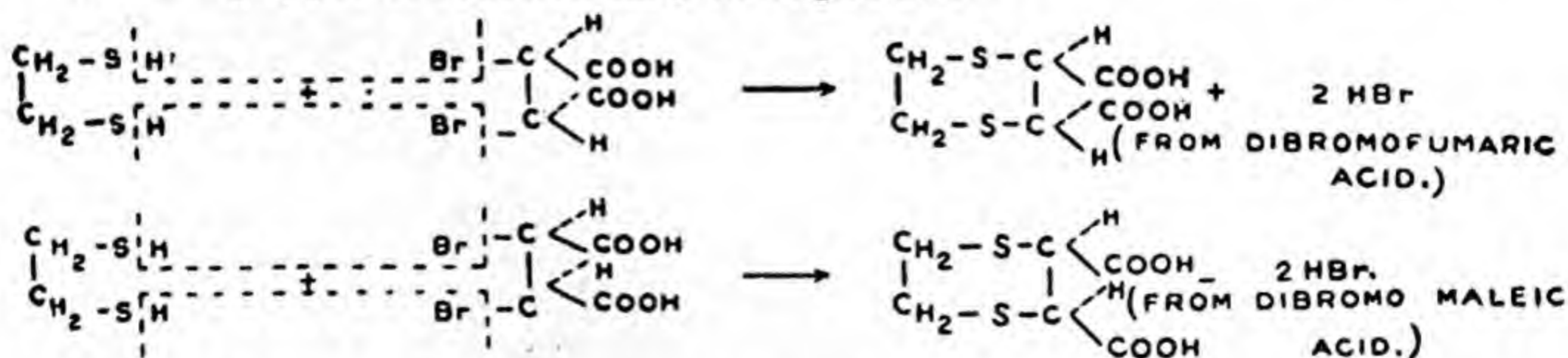
respectively.

Attempts have also been made to condense Benzalacetone with Phenylacetamide, Chloroacetamide,  $\omega$ -Cyanoacetophenone, etc., but with only a partial success. Further experiments with other compounds having a reactive methylene group, e.g. Nitroacetamide, Acetoacetamide, Bromo- and Iodo-acetamides, Cyanoacetone, and  $\beta$ -diketones have also been undertaken.

# 82. Cis-trans isomerism in closed ring compounds having two sulphur atoms in the nucleus.

CHITTARANGAN BARAT, Calcutta.

Dibromo succinic acid occurs in two different isomeric forms according as it is obtained by brominating Fumaric or Maleic acids. The assumption therefore, that they still retain their steric characteristics, is justifiable. If now they are made to condense (after protecting the carboxyl groups, in the form of a salt or an ester,) with Ethylene Mercaptan, the following types of reaction may be expected:—



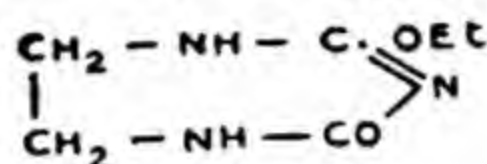
The condensations have actually been effected in the presence of Sodium Ethoxide, in alcoholic suspension, (the mercaptan working best as an alkali mercaptide). The products of condensation, though different, have not yet been obtained in a sufficiently pure form.



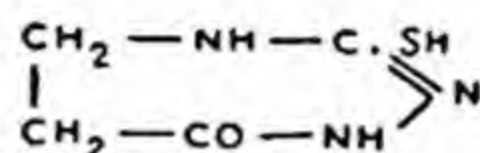
83. Cis-trans-isomerism in ethyl-carbethoxy—thiocarbamate. Synthesis of four-, five-, six- and seven membered heterocyclic compounds from ethyl-carbethoxy-thiocabamate.

P. C. GUHA and N. C. DUTT.

Ethyl-carbethoxy-thiocarbamate has been isolated in two isomeric forms, one melting at 44°C. and the other at 144°C, and the latter has been found to be convertible into the former by boiling with water containing a drop of hydrochloric acid. With ethylene diamine the lower melting variety gives a compound of the following formula :



it is insoluble in alkali, whereas the higher melting variety gives a compound of the following formula :



it is soluble in alkali.

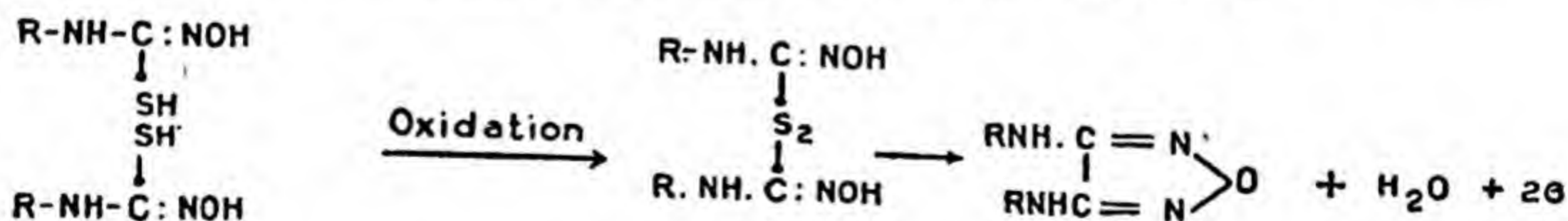
Ethyl-carbethoxy-thiocarbamate has been made to react with aromatic amines, hydrazine, phenylhydrazine, urea, phenylurea, thiourea semicarbazides, ditamines, and ortho-phenylene diamine and thus a large number of interesting hetero-cyclic cyclic compounds have been obtained.

84. Action of hydroxylamine upon mustard oils : formation of—dianilido-furo-(a : a')-diazoles.

P. C. GUHA and M. N. CHAKLADAR.

Hydroxylamine reacts with mustard oils to yield unstable intermediate hydroxy-thiocarbamides thus.—

$\text{R} \cdot \text{N} : \text{C} : \text{S} \cdot \text{NH} \cdot \text{OH}$   $\text{RNH} \cdot \text{CS} \cdot \text{HNHOH}$ , two molecules of which get easily decomposed even at the ordinary temperature to yield furo-(a : a 1)-diazoles with the separation of sulphur and water thus :—



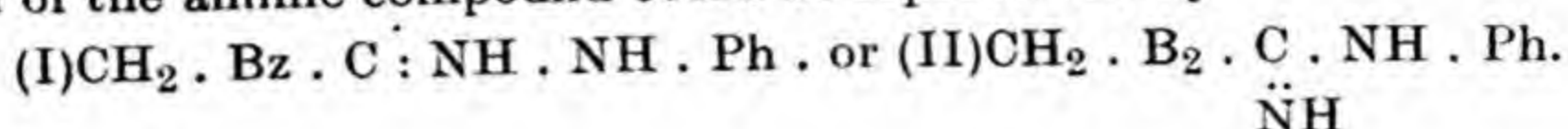
85. The union of benzoylacetone nitrile with organic bases in the presence of salicylaldehyde. Part II.

PANCHAPAKESA KRISHNAMURTI.

Aniline, p-Toluidine and 1 : 3 : 4 Xylidine react in a way similar to piperidine (J.C.S. 1927-128-1349) with benzoylacetone nitrile. Improved yields were obtained by using a few drops of piperidine in the above-mentioned reactions. Ortho- and meta-Toluidines, as well as mono-methyl aniline, p-brom aniline and methyl anthranilate were unreactive. This behaviour seems to be similar to that recently observed with nitro styrene (Worrall, J.A.C.S., 1927-49-1598). The aniline and p-Toluidine compounds readily yield mono-hydrochlorides, diacyl derivatives, and brightly-coloured iso-nitroso derivatives. The latter, on benzoylation,



give only the benzoyl derivatives of the primary amines. The constitution of the aniline compound could be represented by



86. Colour of complex diazoles.—Part III. Double quinonoid structure—the real chromophore.

GOPAL CHANDRA CHAKRAVARTI.

All attempts to correlate colour with the constitution of compounds containing fused pyrrol-iminazole or pyridine-iminazole ring systems have so far been unsuccessful. Hewitt's rule and its modification by Watson and his co-workers are not sufficiently elastic to explain the colour of these nitrogenous bodies. But when the theory of quinonoid structure is extended to heterocyclic compounds like pyrrol and pyridine, a ready explanation of the cause of colour in these condensed systems is at once available. It is found that all the known coloured condensed pyrrol-iminazole or pyridine-iminazol derivatives may be represented as having a double quinonoid pyrrol or pyridine nucleus in them whereas the colourless bodies either do not possess this structure, or if they do possess it, their chromophoric effect is neutralised by the presence of other hypsochromic groups. Hence it is suggested that the presence of a double quinonoid pyrrol or pyridine ring is necessary so that systems containing fused pyrrol or pyridine-iminazole skeletons may develop visible colour.

87. On the interaction of sulphuric acid and bromine on ethylbenzylidenediacetate.

B. M. GUPTA *and* S. C. ROY, Lucknow.

With a view to obtain  $\alpha$ -bromo derivatives of variously substituted ethyl glutarate, ethyl benzylidenediaceoacetate was treated with concentrated sulphuric acid and bromine. A crystalline compound melting at  $159^{\circ}\text{C}$ . having the empirical formula  $\text{C}_{17}\text{H}_{19}\text{O}_6\text{Br}$  was obtained. By studying the products of hydrolysis and oxidation, the constitution of the compound has been fixed as Ethyl  $\alpha\alpha'$ -diaceo- $\alpha$ -bromo- $\beta$ -phenylglutaric acid ester. This formula has been further confirmed by the study of the product of its interaction with aniline, which is a crystalline compound having the empirical formula  $\text{C}_{22}\text{H}_{25}\text{O}_4\text{N}$  and melting at  $131^{\circ}\text{C}$ .

### 88. Preparation of P. chloraniline.

K. HABIB HASAN, Hyderabad (Deccan).

Chattaway and Orton (1901) described a method of chlorinating acetanilide by bleaching powder in glacial acetic acid. A good yield of O. and P. compounds is obtained. On hydrolysis of the anilides the yields claimed for both anilines are not obtained nor the method of separating P. chloraniline is suitable. The causes of this loss had been the subject of this paper which will be described.

### 89. Wandering of groups during brominations.

M. G. SRINIVAS RAO, C. SRIKANTIA *and* M. SESHA  
IYENGAR, Bangalore.

Work continued—(*vide* Reports, Science Congress, 1926—page—147) with 5-nitro 4-methoxy B-resorcylic aldehyde, which on monobromination yields a normal brom-nitro-aldehyde; but this on further bromination apparently rearranges to give a dibrom-nitro derivative, in which



the aldehyde is absent. The second phenolic group in the last was ethylated and the product thus obtained was found to be identical with,

- (1) the nitro derivative of tri-brom resorcinol, in which both the phenolic groups had alternatively been alkylated with methyl and ethyl iodides respectively, and
- (2) the dibrom (ethylated) derivative of 4-nitro resorcinol 3-methyl ether, in which the nitro-group is in the same position as in the original nitro-aldehyde mentioned first.

From these and a few other experiments the authors are led to conclude that the nitroxyl group has wandered during bromination. Work on similar and allied compounds is under way in order to gather more evidence in favour of this conclusion, since such wandering of nitroxyl is not common.

#### 90. Para-aminophenylstibinic acid and its amine salts.

SUDHIR CHANDRA NIYOGY, Calcutta.

The complex nature of Phenyl Stibinic acid and its derivatives has been held by Schmidt (Ber. 55, (1922) 697) while Macallum (J. Ind. Chem. Soc. 42, (1923) 468 T.) maintains from molecular weight determinations that they are simple molecules. The former view seems to be correct from the facts:—

- (1) They lose all, excepting one molecule of water, when kept in vacuo over Sulphuric acid, showing that only one molecule of water is present as water of constitution, and are therefore of the type  $\{(3C_6H_5 \cdot SbO_2)H_2O\}2H_2O$ , or  $\{(3C_6H_5 \cdot SbO_2)H_2O\}3H_2O$ .
- (2) They dissolve completely in  $\frac{1}{3}$ rd their equivalent of alkali giving a solution neutral to litmus, which, however, turns acid on keeping, and takes up the full requisite amount of alkali gradually, yielding a neutral solution which remains so even on keeping or heating.

Hence it is concluded that these compounds, instead of being formed by the replacement of one of the hydroxyl groups of o-Antimonic Acid by Aryl radicals, are produced by a complex association of 3 molecules of Aryl stibinic acid, which gradually breaks up into individual molecules with KOH or NaOH, while LiOH gives the product  $2Ar \cdot Sbo$ , with varying amounts of water. With a view to settle the question of the constitution of the Aryl stibinic acids, amine salts were prepared by adding the requisite amount of the corresponding amine to an aqueous suspension of p-amino stibinic acid, which dissolves readily (in a few cases by slight warming) filtering, and precipitating the salt with alcohol. The following salts with p-aminostibinic acid have been prepared: Methylamine, Dimethylamine, Trimethylamine, Ethylamine, Diethylamine, Triethylamine, Propylamine, Isobutylamine, Iso-amylamine, Benzylamine and Phenyl-ethylamine. Analytical data obtained show that they contain 3 molecules of Aryl stibinic acid and one molecule of the base which corroborates the view held by Schmidt (loc. cit). The physiological actions of these compounds are now being investigated.

#### 91. The essential oil from the flower-heads of *Cymbopogon coloratus* Stapf.

P. PARAMESWARAM PILLAI.

The essential oil from the flower-heads of *Cymbopogon coloratus* Stapf has been described and is shown to contain 1-camphene (app. 15 per cent.) 1-limonene (5 per cent.) 1-borneol (8 per cent.) geraniol (10 per



cent.) camphor, a mixture of sesquiterpenes one of which gives a nitrosate (m.p.  $154^{\circ}\text{C}$ ) and a nitrosochloride (m.p.  $171^{\circ}\text{C}$ ) and is probably  $\alpha$ -caryophyllene.

## 92. Jute-seed oil.

NIRMAL KUMAR SEN.

The brown seeds of *Corchorus capsularies* yield 14.73% of oil by extraction with petroleum ether. The refined oil show a sapon. value 184.4, Iodine value (Hubl's) 102.6, acetyl value 27.3, acid value 1.5, Reichert Meissel value 0.16, Hehner's value 94.1, Glycerol 8.12% unsaponifiable matter 2.77%. The mixed fatty acids (free from unsaponifiable matter) of the oil are a white solid mass; has the following properties: m. p.  $31.5\text{--}32^{\circ}\text{C}$ , Titre  $29.9^{\circ}$  Iodine value 113.44, neutralisation value 200.2, mean mol. wt. 280.2, and contain 20% solid and 80% liquid acids (Twitchell). The liquid acids give no ether-insoluble compound by bromination and are composed of 70.02% Oleic and 29.98% Linolic acids and yield di and tetrahydroxystearic acids respectively by oxidation with alkaline permanganate. The solid acids melt at  $50\text{--}52^{\circ}\text{C}$  and yield "Crude Archidic acids" melting at  $74\text{--}75^{\circ}\text{C}$ . The unsaponifiable matter contains phytosterol. When purified the oil is suitable as a food and is also satisfactory for burning purposes.

## 93. Properties and composition of sandal seed oil.

M. SREENIVASAYA and N. NARAYANA.

Sandal seeds contain 50–55 per cent. of a thick viscous oil. On exposure to light, the oil spontaneously thickens to a resinous mass; at  $130^{\circ}\text{--}140^{\circ}\text{C}$ . sulphur is absorbed resulting in a plastic rubber-like compound. On saponification with alcoholic potash a white resinous mass is thrown out which has very high iodine value. An ether extracted oil has the following physical and chemical constants:—

Refractive index at  $60^{\circ}\text{C}$ . 1.4790; Specific Gravity, at  $30^{\circ}\text{C}$ . 0.9304; iodine value 130–140; Sap. Value 185–195; acid value 20–25; Hehner number 96–97; Richert-Meissel value 1.5; Polensky number 0.2–0.3 Mean mol. weight of the mixed fatty acids 288.5.

## 94. Indian Cubeb oil.

V. P. SHINTRE.

The fruits grown in the Mysore Province gave on distillation with steam 7.5 per cent. of an essential oil. The oil has been found to contain *d*-sabinene (28 per cent.) *d*-terpinene and cineol (15 per cent), *d*-terpinenol-4, *d*-terpineol, an unidentified primary alcohol, 1-cadinene and another sesquiterpene. Another sample of oil was found to contain *dl*-sabinene and the other constituents were the same as in the first sample described.

## 95. The constituents of *Sweertia chirata*.

A. JANAKI RAM.

*Sweertia chirata*, the well known valuable indian medicinal plant has been partially examined by Sahiar in 1914 and Subramaniam in 1924. A more extensive investigation of the same has now been undertaken.

By steam distillation of the alcoholic extract, a crystalline acid, a phenol and isoamyl alcohol have been obtained.

The residual resin insoluble in water has yielded an acid M.P.  $312^{\circ}\text{C}$  and a neutral body M.P.  $133^{\circ}\text{C}$ .

(The non-volatile portion soluble in water contains an acid M.P.  $193^{\circ}\text{C}$ .)



96. Thevetin : a crystalline glucoside from the seeds of *Thevetia neriiifolia*. Part I.

P. RAMASWAMI AYYAR.

The defatted seed-kernels of the yellow oleander yield to alcohol about 1.5 per cent. of a glucoside which has been obtained in the form of glistening white plates melting at  $215^{\circ}$  after softening at  $190^{\circ}$ .

Analysis gave the following values *C*, 56.2; *H*, 7.2; *O*, 36.6 hydroxyl 2-4, methoxyl 3.0.  $[\alpha]_D^{31} = -39.2^{\circ}$ .

Hydrolysis with 1 per cent. sulphuric acid gave 57 per cent. of sugar, and 48 per cent. of Non-sugar.

$[\alpha]_D^{31}$  for the sugar was  $+22.7^{\circ}$ ; and an osazone was obtained melting at  $205^{\circ}$  and a pentacetate melting at  $180^{\circ}$ .

From the non-sugar, an acid was obtained melting at  $150^{\circ}$  and having an equivalent of 425.

97. On lignoceric acid from the seeds of *Adenanthera pavonina*. Part I.

P. RAMASWAMI AYYAR.

So far the main sources of lignoceric acid in nature have been beechwood tar, and peanut oil. It has been found that the above seeds yield 14% of a fixed oil equivalent to 13% of mixed acids. From the latter pure lignoceric acid  $C_{24}H_{48}O_2$  melting at  $80-81^{\circ}C$  has been prepared with a yield of 1.5 per cent. on the seeds.

The acid on bromination by Volhard's method yields a bromo-acid melting at  $70-71^{\circ}C$  whose bromine content and equivalent weight correspond to the formula  $C_{24}H_{47}BrO_2$  and the lignoceric acid thus appears identical with the acid previously obtained from other sources. The constitution is being investigated.

98. On Rubiadin.

PRAFULLA CHANDRA MITTER, MONMOHAN SEN, PRAFULLA KUMAR PAUL and PRIYALAL GUPTA, Calcutta.

In the Bombay Session of this Congress (1926) one of us (M) drew the attention of the Congress to the fact that the product of condensation of cresorsellenic acid with benzoic acid which was supposed, in an earlier communication to the Congress, to be Rubiadin, melts on repeated crystallisation at  $265^{\circ}-266^{\circ}C$  and therefore it could not be Rubiadin. Unfortunately the mistake in the earlier communication has been allowed to continue in the proceedings.

It has now been found that the 1-methyl-2-4-dihydroxy-anthraquinone gives a diacetyl derivative M.P.  $181^{\circ}-182^{\circ}C$  which on de-acetylation melts at  $265^{\circ}-266^{\circ}C$ , so that there cannot be any doubt that Rubiadin is not 1-methyl-2-4-dihydroxy anthraquinone. Recently Stauder and Adams (J. Amer. Chem. Soc. 1927, pp. 2043) have come to the same conclusion. The 1-methyl-2-4 dihydroxy-anthraquinone prepared by them melts at  $251^{\circ}C$  and the acetyl derivative (which they have not analysed) melts at  $176^{\circ}C$ . Evidently S. and A. had a very impure product in their hands due no doubt to the large number of stages involved in their synthesis.

We have also succeeded in synthesising Rubiadin itself by condensing 2-6-dihydroxy-p-toluic acid with benzoic acid (Schunck and Marchlewskis' original method: T, 1894, 65, 182). The 3-methyl-2-4-dihydroxy anthraquinone melts at  $290^{\circ}C$  and its acetyl derivative melts at  $225^{\circ}C$ .

The oxy-methyl-anthraquinones present in nature have hitherto been regarded as derivatives of either  $\alpha$ - or  $\beta$ -methyl anthracene. It now seems



as if there is no  $\alpha$ -methyl anthracene derivative among the natural products for within the last few years substances like chrysorobin, chrysophanic acid, Rhein and Emodin which at one time or had been regarded as  $\alpha$ -methyl anthracene derivatives have been proved to be  $\beta$ -methyl anthracene derivatives. Rubiadin is here proved to be a  $\beta$ -methyl anthracene derivative.

One of us (M) is now engaged with Asoke Kumar Sen in the synthesis of Munjisthin which probably bears the same relation to rubiadin as Rhein to chrysophanic acid.

## 99. Curcumene.

B. SANJIVARAO.

This hydrocarbon, occurring in the essential oil from the rhizome of *Curcuma aromatica* Salisb. and characterised by a trihydrochloride (m.p. 84–85°C and a nitrosate (m.p. 100–101°C) has been found to be a mixture of two sesquiterpenes which have been separated and the names  $\alpha$  and  $\beta$ -curcumene proposed.  $\alpha$ -curcumene is characterised by the nitrosate (m. p. 100–101°C) and has been obtained by a series of reactions from the nitrosate and has the following constants:—

$$\left(d_{30}^{30} = 0.8633; n_D^{30} = 1.4944; [\alpha]_D = -35.4^\circ [R]_L = 68.86 \cdot 124 - 126 / 10 \text{ mm.}\right)$$

Its molecular refraction shows it to be a monocyclic sesquiterpene. It takes up only two atoms of bromine and gives a liquid monohydrochloride and does not give a naphthalene derivative on treatment with sulphur.

$\beta$ -curcumene is obtained from the solid trihydrochloride and gives a liquid hexabromide and an excellent yield of the solid trihydrochloride.

$$\left(d_{30}^{30} = 0.8625; n_D^{30} = 1.4888; [\alpha]_D = -37.5^\circ [R]_{LD} = 68.23\right).$$

Some experiments with these sesquiterpenes have been described.

## 100. Delignification of jute fibre.

JOGENDRA KUMAR CHOWDHURY and RAMENDRA KUMAR DAS,  
Dacca.

The object of the following work is to remove incrusting matters of jute with least possible injury to the structure of the fibres.

The usual methods of removing lignone complex from lignocelluloses reduce jute to ultimate fibres or cells and also attack more or less the cellulose complex. In creosote, however, a solvent has been found which dissolves lignone matter without similarly affecting cellulose. Owing to the acidic nature of creosote, the fibre however becomes brittle, the cellulose being evidently reduced to hydrocellulose. This adverse effect has been overcome by the addition of basic substances such as pyridine. A sample of raw jute whose lignone and pentosan contents were 19.69% and 11.0% respectively, when treated with creosote mixed with 10% pyridine under optimum conditions of temp. & pr. Yielded a fibre which was of apparently good tensile strength and whose lignone and pentosan contents were only 4.4% & 8.67% respectively. On treatment with alkali, the lignone and pentosan contents were further reduced to 2.5% and 4.09% respectively. The fibre thus obtained gives all the characteristic microscopic colour reactions of cellulose and has fairly good tensile strength.

Incidentally, the theory of Wislicenus, that in lignocelluloses,



cellulose and lignone complexes are held together by forces of surface energy, is supported.

101. *Excoecaria agallocha* as a source of power alcohol.

HEMENDRA KUMAR SEN, SINDHU BHUSAN GHOSH and PATIT PABAN PAL, Calcutta.

In continuation of our search for a suitable material for the production of power alcohol, we were led to the investigation of the sawdust from a particular variety of wood. *Excoecaria agallocha* which grows abundantly in Sundarban tracts and is now being used plentifully for the match industry and also for making cheap packing cases. Whilst with most species examined before, 22·24% of reducing sugar was found to be the maximum production after hydrolysis by Simonsen's process, namely, digestion with very dilute sulphuric acid under 9 atmospheric pressure, with *Excoecaria agallocha* the yield of sugar was about 40% of the weight of dry sawdust. Of this about 70% was readily fermentable, giving approximately 39 gallons of absolute alcohol, a figure practically double of what was obtained in the past. With appropriate figures of cost, a gallon of absolute alcohol from *Excoecaria agallocha* would work out at 6·05 annas. Given a continued supply of this wood, there is thus an excellent prospect of power alcohol industry in the province of Bengal.

102. The constituents of *Plumbago Zeylanica* Linn.

M. C. TUMMINKATTI.

'Plumbagin,' the active principle of the drug, has been isolated in a pure form. It forms orange yellow silky needles melting at 78°C. It is soluble in most organic solvents and in alkaline solutions with formation of a crimson or pink colour. The combustion and the molecular weight determination indicate an aromatic ring compound. The deep red colour with ferric chloride solution indicates a phenolic hydroxyl group in the compound. The benzoyl derivative melts at 146°C. Further physical and chemical properties are being studied with a view to determine the constitution.

103. A micro-method for the analysis of proteins.

N. NARAYANA and M. SREENIVASAYA.

Van Slyke's well-known method of protein analysis has been extended and modified for dealing with 100 to 200 milligrams of substance, a twentieth of the quantity usually employed for a micro-analysis. The precipitation of the hexone bases by phosphotungstic acid, which is affected by the presence of salts, is controlled by the effective removal of the hydrochloric acid from the protein hydrolysate in vacuo over freshly burnt lime. Arginine is estimated by flavionic acid and histidine by bromination. Total mono-amino and diamino nitrogen is estimated by the Van Slyke micro-apparatus. Cystine is estimated by a micro-estimation of sulphur after Pregl. Tyrosine is determined colorimetrically.

104. Studies in sap analysis.

M. SREENIVASAYA and B. N. SASTRY.

(1) Carbohydrates in saps.

The estimation of Sugars in saps is complicated by the presence of interfering impurities such as tannins, gallic acid, dextrans, proteins and similar bodies. Precipitating agents like basic lead acetate, dialysed iron, fibrous alumina, mercuric chloride, etc. have proved unsatisfactory



in one way or another. A very suitable method consists in the preliminary removal of dextrans and the greater part of the proteins by an addition of 10 volumes of 95% alcohol containing a little ammonia. The alcoholic filtrate is concentrated on a waterbath, tannins, etc., are eliminated by dialysed iron, and the clear filtrates used for the sugar estimations by Bertrand's method. The direct reducing sugars are estimated as dextrose, the Citric acid hydrolysis gives cane sugar, and the HCl hydrolysis gives Maltose. Invertase and Maltase are also being tried for the estimation of Sucrose and Maltose.

The saps can also be absorbed on fat free filter paper, extracted by 95% alcohol containing a little Ammonia and the alcoholic extract treated as above. This modification gives excellent results.

105. A comparative study of different methods for the estimation of pentosans.

D. D. DESHAPANDE and ROLAND V. NORRIS, Bangalore.

A comparison of the phloroglucin method of Tollens, the barbituric acid method of Jagger, Jelle's bisulphite-Iodine method and various colorimetric methods.

106. The estimation of pyruvic acid.

B. H. KRISHNA.

Description of a method suitable for estimation of small quantities of pyruvic acid, from 2 to 20 mgms, in biological fluids. The acid is reduced to lactic acid by Zinc and  $H_2SO_4$  in the presence of a trace of copper sulphate. The resulting lactic acid is oxidised to acetaldehyde which is estimated by Clausen's method of titration against Iodine. A condensing unit is described by which the aldehyde can be transferred into the receiver by aeration with carbon-dioxide without any water passing into the receiver. The experimental errors involved and the corrections required to allow for these are discussed.

107. The action of tannase on tannic acid.

P. D. DALVI and ROLAND V. NORRIS, Bangalore.

An investigation of the factors influencing the action of tannase derived from *Aspergillus* and other moulds.

108. Diastatic activity of spiked sandal leaves.

M. SREENIVASAYA and B. N. SASTRY.

The excessive accumulation of starch in the leaves and stems of spiked sandal has been accounted for by the supposition that the poor diastatic activity of spiked materials does not allow the rapid translocation of the starch. Experiments carried out to verify this point showed us that, contrary to the above supposition, the starch hydrolysing capacity of the spiked leaves is invariably greater than that of healthy leaves. This has been further confirmed by the enzyme analysis of saps. The greater diastatic activity of spiked leaves does not appear to be due to the presence of any associated activator. The starch hydrolysis has been followed and it has been shown that starch splitting by the spiked-leaf-diastase and healthy leaf-diastase are different, the saccharifying capacity of the former being greater.



## 109. Physical chemistry and biochemistry of haemolysis.

K. C. SEN, Allahabad, and S. K. BASU, Calcutta.

A large amount of work has been done on the haemolysis of red blood corpuscles by haemolytes, but no satisfactory explanation has yet been given. In order to find out a suitable explanation, the present authors have carried out a large number of experiments on this subject. The experiments have been divided into two main parts, namely, first, a colloid chemical study of the corpuscle constituents such as lecithin, cholesterol, hemoglobin and albumin, and secondly, the homolysis of sheep's red blood corpuscles by bile salts and their inhibition by normal serum and egg protein. The haemolysis of sheep's erythrocytes and horse erythrocytes by heavy metals and by acids, as well as the behaviour of saponin, of alkali and of hypotonic solutions as hemolytes have been discussed. The following summary gives the main results obtained.

1. Haemoglobin forms a negatively charged colloid in water. Acids sensitise and alkali peptises the sol. Towards electrolytes it behaves like a typical hydrophobic sol. The importance of keeping blood alkaline in normal health is obvious because otherwise the hemoglobin would get precipitated and hence would lose its power of forming oxi-hemoglobin.

2. Haemoglobin sol is sensitised by alcohols, lecithin, albumin and saponin. In alkaline solution, however, lecithin does not sensitise the sol. Mixtures like barium chloride and caustic potash and potassium chloride and caustic potash have a considerable antagonistic action. Saponin precipitates the hemoglobin sol in slightly acid medium, but not in alkaline medium. Soaps (alkali) have a great peptising action. Sodium taurocholate has also a peptising action.

3. The lecithin sol behaves like a hydrophillic colloid. With heavy metals, haemoglobin has a sensitising action.

4. Lecithin stabilises cholesterol considerably, but in presence of excess of cholesterol, it is itself sensitised.

5. Saponin and sodium taurocholate peptise lecithin.

6. An experimental study has been made on the inhibitory effect of blood serum and egg protein on glycocholate and taurocholate hemolysis of sheep's red blood corpuscles. It is shown that this effect is only a special case of the general antagonistic action between a sensitising and a peptising agent in diphasic systems.

7. It has been found that glycocholate is a much stronger hemolyzing agent than taurocholate.

8. The mechanism of the haemolysis of red blood corpuscles by haemolytes has been discussed. It is shown that the corpuscle membrane is in the colloidal state, and haemolysis may occur either due to an extreme coagulation whereby cracks will be formed, or by extreme peptisation whereby all the particles will go into apparent solution thus loosening the whole structure. In some cases it may be due to a pure osmotic effect where a mechanical rupture of the membrane is possible. This view will explain the following cases:—Haemolysis by hypotonic solutions, by acids or alkali, by saponin, soap and bile salts, by narcotics and possibly that due to bactericidal action.

## 110. A biochemical investigation of healthy and spiked sandal twigs.

M. SREENIVASAYA and D. A. RAMA RAO.

A systematic analysis of twigs from two sandal areas reveals the interesting facts that the spiked specimens contain more nitrogen and probably more carbohydrate material than the healthy tissue but less of some of the mineral constituents than the healthy ones. The starch content of the alcohol extracted residue is under investigation.



111. Studies in Chalam diastase. Part 1: electrodialysis and electro-osmosis of Chalam diastase (Preliminary note).

D. NARAYANAMURTI and ROLAND V. NORRIS, Bangalore.

By electrodialysis *chalam* malt diastase can be purified and considerably increased in activity. The ash and protein content are much reduced by this method.

An attempt was made to test the two-enzyme theory of diastase by electro-osmotic experiments. Preliminary experiments conducted in a 5 celled apparatus indicate some evidence in favour of the theory, the ratio, liquifaction power, saccharification power, being different in the different fractions.

Some electro-ultrafiltration experiments with diastase are also described.

112. Kinetics of diastatic action.

D. NARAYANAMURTI and ROLAND V. NORRIS, Bangalore.

The kinetics of the hydrolysis of starch by *chalam* diastase is discussed and an explanation for the divergencies in the results of various observers sought for. Experiments on the hydrolysis of potato, rice and *chalam* starches and oyster glycogen are described. In agreement with other observers glycogen is found to be the most resistant. Experiments designed to elucidate the difference are described and the probable causes for the variation in the resistance of the different starches discussed.

113. A bio-chemical study of spike disease of sandalwood.

A. V. V. IYENGAR and ROLAND V. NORRIS, Bangalore.

A comparison of the composition of the leaves of the healthy and diseased trees and a physico-chemical study of the leaf sap. Carbohydrates and nitrogen are both increased in the diseased leaf while a diminution occurs in some of the mineral constituents.

114. Effects of Hydrogen-ion concentrations on rice cultures.

S. K. MITRA and LOKENATH PHUKAN, Jorhat Assam.

Effects of hydrogen-ion concentrations on rice cultures were studied with Knop's Solution as the standard nutrient solution and with hydrochloric acid and caustic soda as the adjusting mediums the concentrations of which varied from 0.001% to 0.01% and 0.001% to 0.05% respectively. The *PH* values of the solutions ranged from 3.0 to about 8.4. The experiment was continued with one-month old seedlings for a fortnight and the total length of roots in millimeters was taken as the criterion of growth.

The results were as follows:—

1. The seedlings showed strong acid toxicity at a concentration of 0.002% HCl, whereas higher concentrations were distinctly inhibitory to root growth. With the addition of alkali, the roots developed far better and the highest root development was shown at a concentration of 0.3% NaOH.

2. A definite relationship was found between the hydrogen-ion concentrations of the culture solutions and their corresponding root lengths, which showed a steady increase with the higher *PH* values. *PH* 3.9 was distinctly toxic whereas *PH* 3.3 was extremely toxic to root growth. At acidities less than *PH* 6.0, the development of roots was below normal but beyond this it was quite satisfactory. The highest root growth was



attained at *PH* 7.9 but further on a drop was shown at *PH* 8.4 which is, however, not quite confirmatory and requires further experimentation.

115. Effects of Shive's three-salt nutrients on rice seedlings.

S. K. MITRA and LOKENATH PHUKAN, Jorhat, Assam.

Following Shive's procedure an experiment on the effects of the three-salt nutrients of mono-potassium phosphate, calcium nitrate and magnesium sulphate was tried on the development of roots in rice seedlings. The nutrient solutions were arranged to give all possible combinations in variations of one-tenth to eight-tenths of the total osmotic concentration of 1.75 atmospheres, for each of the three salts used. The results of the experiment were as follows:—

1. The culture showing the highest root development had five-tenths of its total osmotic concentration due to monopotassium phosphate, two-tenths due to magnesium sulphate and three-tenths due to calcium nitrate. Similarly, other high root developments were characterised by high concentrations of monopotassium phosphate and low concentrations of calcium nitrate and magnesium sulphate.

2. The culture showing the lowest root development had three-tenths of its total concentration due to mono-potassium phosphate, five-tenths due to calcium nitrate and two-tenths due to magnesium sulphate. The region of low root development was characterised by low concentrations of mono-potassium phosphate and high concentrations of calcium nitrate or magnesium sulphate or both.

3. The best and the worst cultures contained the metallic ions of magnetism, calcium and potassium in the proportions of 0.56 : 0.43 : 1.00 and 0.93 : 1.20 : 1.00 respectively.

116. On a new device for maintaining better vacuum in the vacuum pan apparatus.

N. G. CHATTERJEE.

117. A history of chemistry in the Punjab.

H. B. DUNNICLIFF and RAMA KRISHNA BAHL, Lahore.

The paper records the development of the subject from 1849 to the present time in Geology, Medicine, Agriculture and Education.

118. The action of sulphuretted hydrogen on potassium chromate solution.

H. B. DUNNICLIFF and CHAMAN LAL SONI, Lahore.

In dilute solutions (2-15%  $K_2CrO_4$ ) the colour changes from yellow to green with evolution of heat. Chromium is recovered quantitatively as hydroxide and the potassium is obtained as pentasulphide and thio-sulphate.

119. The action of substituted amines on camphoric anhydride. Bromocamphoranic acids and camphorobromophenylimides.

MAHAN SINGH, RAM SINGH and KISHEN LAL, Lahore.

The reaction





is dependent on the nature of the Group *R*. Bromanilines have been condensed with camphoric anhydride. The yields of the imides are, *p.*, 40%, *m.*, 25%, *o.*, 5%. The substances are optically active and their rotations have been found in various solvents.

120. The solubility of mercuric bromide in ethyl alcohol.

KISHEN LAL and H. B. DUNNICLIFF, Lahore.

The values found by the method of Chugaev and Khlopin (*Z. Anorg. Chem.* 1914, p. 159) are consistently higher than those recorded by Timofeiew.

121. The causes and prevention of saline efflorescences on Masonry. (Preliminary Note.)

H. B. DUNNICLIFF and RAMA KRISHNA BAHL, Lahore.

The nature of a number of efflorescences has been examined and attempts made to find if any changes which should cause such efflorescences are developed during the baking of the bricks.

122. Compounds of hexamethylene tetramine with certain salts of silver and other metals and the influence of anionic volume on the capacity for association by the central positive atom.

PRIYADA RANJAN RÂY and JYOTIRMOY DAS GUPTA, Calcutta.

It has been established by Ephraim (*Ber.* 53, 548, 1920; 54, 973, 1921) that the capacity of a cation to associate with neutral molecules increases with the anionic volume. With a view to further test the validity of this conclusion the authors have prepared a number of well-crystallised compounds of hexamine with various silver salts like cyanide, cyanate, thiocyanate, perchlorate, chromate, dichromate, molybdate, tungstate, sulphate and selenate. From a study of the nature and composition of these compounds as well as of some other hexamine silver salts previously described by others, it was concluded by the authors that Ephraim's generalization holds good also in the case of hexamine compounds. Anomalous result in the case of silver fluoride is attributed to the formation of a complex anion of silver and fluorine due to polymerization. With a common anion the capacity of the cation for association has also been studied in the case of certain newly prepared hexamine compounds with cyanides of copper, cadmium and silver. The composition of these latter compounds has also been explained in the light of Ephraim's conclusion. The failure of tellurate, phosphate, borate, iodate, arsenite and arseniate of silver to associate with hexamine molecules has also been accounted for on similar grounds. All the hexamine compounds described in this paper have been obtained by a method based on the principle of substitution from an ammoniacal solution of the salts.

123. Active aluminium.

G. SAMBAMURTI and N. L. NARASIMHAM, Rajahmundry.

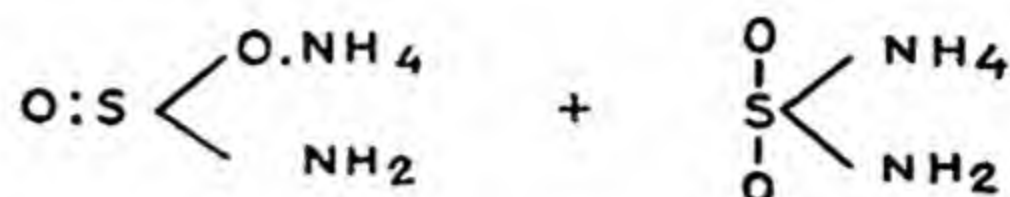
Aluminium becomes activated by amalgamation and the activated metal serves as a good reducing agent in a neutral medium. The activated metal readily oxidises in moist air having traces of CO<sub>2</sub>.



124. The interaction of sulphur dioxide and ammonia.

G. SAMBAMURTI and M. N. L. NARASIMHAM, Rajahmundry.

Dry sulphur dioxide and dry ammonia interact producing two isomers of the constitution.



125. Equilibrium diagram of the system arsenic-antimony.

Q. A. MANSURI, Aligarh.

The system has been studied both thermally and microscopically with Arsenic and antimony alloy in all proportions. The curve gradually rises from the melting point of antimony to that of arsenic and the diagram is similar to that of copper and nickel. The two metals form a continuous series of mixed crystals which are hexagonal in shape.

126. The system Water—Potassium nitrate—calcium nitrate at 25°C.

MOHAMMAD ABDUL HAMID and RAM DAS.

On account of the relatively great electroaffinity of the nitrate ion, the formation of double nitrates is found to occur in but few cases. These double nitrates are formed only when one of the metals has a valency greater than two or when one metal is of high atomic weight and volume.

The unexpected formation of a double nitrate of Potassium and Barium,  $\text{K}_2\text{Ba}(\text{NO}_3)_4$  [Wallbridge, Amer. Chem. Jour. 32, 251, 1904] led us to conclude the possibility of the existence of similar double nitrates of Potassium with other alkaline earth metals. In the case of Calcium no evidence of double nitrate formation has been found from our investigation of the system  $\text{H}_2\text{O}-\text{KNO}_3-\text{Ca}(\text{NO}_3)_2$  at 25°C.

A number of hydrates of Calcium Nitrate have been reported in literature. Our observations that the only stable hydrate at 25°C is the Calcium nitrate tetrahydrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  agree with those of Basset and Taylor [Jour. Chem. Soc., 101, 576, 1912].

127. Heterogeneous equilibria between the sulphates and nitrates of sodium and magnesium and their aqueous solutions.

MOHAMMAD ABDUL HAMID and AMBA PARSHAD.

The quaternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3-\text{MgSO}_4-\text{Mg}(\text{NO}_3)_2$  has been investigated at 25°C. In addition to the solid phases met with in the ternary systems at this temperature, a new surface appears in the quaternary system which probably represents the saturation field of the lower hydrate or hydrates of Magnesium Sulphate.

128. Iodates of titanium.

PRIYADA RANJAN RAY and HARIBOLA SAHA, Calcutta.

By the action of iodic acid dissolved in nitric acid (1 : 3 by volume) upon freshly prepared titanous acid dissolved in the same solvent, a basic



iodate of titanium has been obtained. The individuality of the substance in question has been established by the fact that the same product was obtained from the liquid phase of varying concentration. It is preferable to regard the compound as a complex tetra-hydroxy di-iodate titanic acid for several reasons. It is converted by heating to 100°C to the proper basic titanium iodate. Salts of complex hydroxy-iodato-titanic acid have also been prepared.

129. A note on a new method of volumetric estimation of mercuric oxide.

PRIYADA RANJAN RÂY and JYOTIRMOY DAS GUPTA,  
Calcutta.

Mercuric oxide completely dissolves in sodium thiosulphate solution in the cold with liberation of an equivalent amount of alkali and formation of the complex mercury sodium thiosulphate. The reaction is a quantitative one and the amount of mercuric oxide in a sample can be easily determined by titrating the alkali disengaged. The excess of thiosulphate present does not interfere with the titration of the alkali. This furnishes a rapid method of evaluating mercuric oxide in commercial samples of the same, in basic salts of mercury and in various medicinal preparations. It has got sure advantages over the potassium iodide method of Rupp and Schirmer (Pharm. Zeit. 1908, 53, 928) being much less expensive; the results however are equally good.

130. Catalytic decomposition of nitrous oxide.

M. S. SHAH.

In the analytical investigation of the reaction ( $C + N_2O$ ) at various temperatures it was found that nitrous oxide decomposes at a lower temperature in presence of charcoal than when heated alone. This suggests that the behaviour of charcoal is catalytic. On examination of the catalytic influence of thoria, alumina, titania and platinum, a similar lowering in the temperature of decomposition of nitrous oxide was observed. Comparison of curves for nitrous oxide decomposed in an hour against temperature in presence of these substances showed that these substances act as catalysts in the order: thoria, charcoal, alumina, platinum black, titania and platinum foil.

131. Interaction between hydrated copper oxide and neutral salt solutions.

M. P. VENKATARAMA IYER.

Hydrated copper oxide thoroughly purified by repeated washing and subsequent electro-dialysis to remove the last traces of alkali is found by electro-osmotic measurements to be positively charged in contact with conductivity water. It develops appreciable quantities of alkali when shaken up with solutions of neutral salts. The pH developed depends upon the effect of the anion and not very much on the cation used. The variation of the electrical charge of the substance with various electrolytes can be correlated to the pH measurements. The total quantity of alkali liberated by repeated shaking of a given quantity of the sample with potassium and barium chlorides has been measured and found to be a constant quantity. The pH, after attaining the value 7.6, remains constant on subsequent shaking with potassium chloride. The sample of



the hydrated copper oxide has been shown to absorb alkalies by measurements of the electrical conductivities of the alkali solution before and after adsorption. The results obtained are in strong support of the theory of the nature of the interface as put forward by Mukherjee.

### 132. Reduction of copper salts to metallic copper by glycerol.

B. K. VAIDYA and C. N. SHAH, Ahmedabad.

On heating glycerol solutions of copper salts, decomposition occurs, whereby metallic copper is precipitated, except in the case of cupric chloride, which yields cuprous chloride.

The temperature at which the reaction occurs is different for different salts. With copper sulphate the reduction takes place at  $210^{\circ}\text{C}$ , with copper nitrate at about  $180^{\circ}\text{C}$  and with copper acetate and copper chloride at  $190^{\circ}\text{C}$ . In all cases an intermediate stage in the reduction, namely, the formation of yellow cuprous oxide, can be marked. The vigour of reduction is considerable in each case, with copper sulphate the action being almost violent.

Besides metallic copper, other products of reaction are, acrolein, acrylic acid and the acid obtained from the decomposition of the respective salts.

The similarity in the nature of the reactions with all copper salts indicates that the glycerol compound of copper is formed in all probability, and this then decomposes into copper, aldehyde and other products. It is also likely that the salts, becoming anhydrous at a higher temperature, remove water from glycerol, thus producing acrolein, but their subsequent reduction to metallic copper is strange.

The reaction is being studied further.

### 133. A new method of preparing hyponitrites and preparation of some new hyponitrites.

P. NEOGI and BIRENDRA LAL NANDI, Calcutta.

In this paper the reducing action of magnesium amalgam on metallic nitrates and nitrites has exhaustively been studied when it has been found that this reaction can conveniently be made a method of preparing hyponitrites. With the help of this method hyponitrites such as those of Na, K, Ca, Sr, Ba and Pb have been prepared and several new hyponitrites such as those of Cd, Zn, Mg, Li, Rb and Cs, have been isolated and analysed. Magnesium hyponitrite has, however, been obtained in solution only. Basic hyponitrites of cadmium and lead have also been obtained. Hydroxylamine is also obtained in all cases of reduction excepting in the case of rubidium and caesium nitrates. This method has the advantage of yielding the hyponitrites *directly* by the reduction of their nitrates and nitrites, whilst previously most hyponitrites were prepared by double decomposition with sodium hyponitrite. The success in the preparation of the hyponitrites lies in the insolubility of the magnesium hydroxide formed during the reaction, whilst caustic Soda which is formed in large quantities in Divers' method of using sodium amalgam is difficult to remove in the case of soluble hyponitrites and reacts with the nitrates of heavy metals precipitating their hydroxides.

Nitrates of other metals do not yield hyponitrites. Copper nitrate gives basic copper nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$  and silver nitrate is reduced to metallic silver. Cobalt and nickel nitrates were reduced to their hydroxides and mercuric and mercurous nitrates yielded the respective oxides. Ammonium nitrate yielded the nitrite, and free dilute nitric acid yielded hydroxylamine which was isolated as the sulphate in the pure condition.



134. A new method of preparing mercury compounds of phenols, phenol-ethers and aromatic amines.

P. NEOGI and MANAS PRASUN CHATTERJEE, Calcutta.

Aromatic compounds of mercury had hitherto been prepared by Dimroth, Pesci and several others by heating the organic compounds with mercuric acetate. Dimroth has reported that mercuric chloride has little or no action on aromatic compounds. P. Neogi and S. Neogi (Trans. Chem. Soc. 1927, pp. 30—37) have however recently shown that a distinct period of induction exists when mercuric chloride and sodium bicarbonate are allowed to act which can be indefinitely prolonged by the addition, amongst other things, of glycerol. Advantage has been taken of this phenomenon in this paper to prepare mercury organic compounds, mostly in the cold, of phenols, phenol-ethers and amines by adding the organic compound to the mixture of mercuric chloride and sodium bicarbonate in the presence of glycerol. In this way mono and dioxy-mercuric-chlorides of phenol, catechol, quinol, resorcinol, phoroglucinol, oreinol, guaiacol, aniline, methylaniline and dimethylaniline have been prepared. In the case of substances not soluble in water alcoholic solutions are taken.

135. A new method of effecting geometrical inversion: Part I: Conversion of maleic into fumaric acid.

P. NEOGI, SUKUMAR NEOGI and MANAS PRASUN CHATTERJEE, Calcutta.

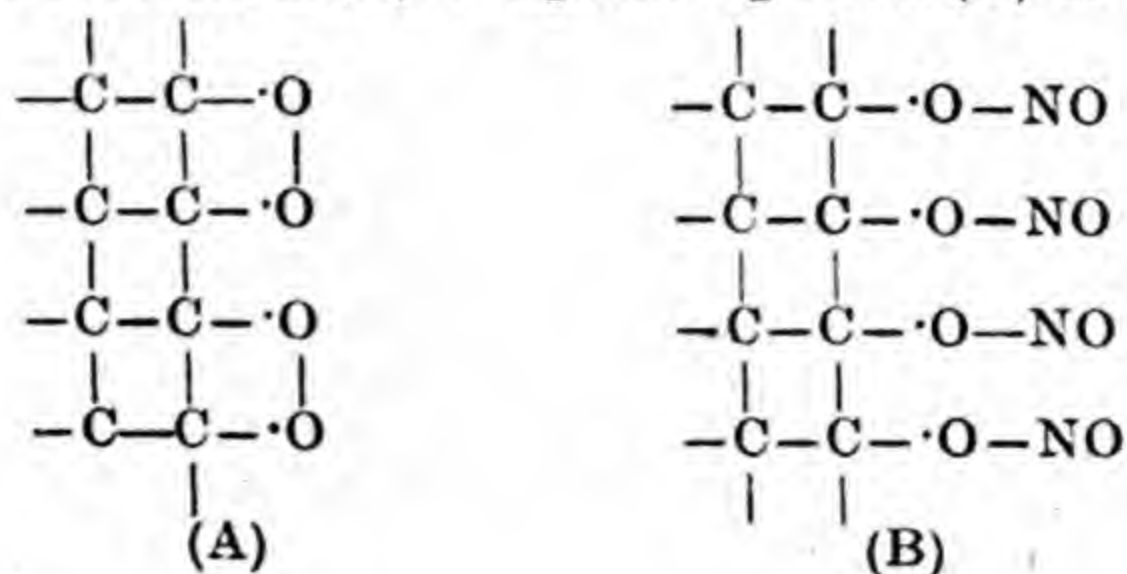
Skraup has shown that maleic acid is converted into fumaric acid by the joint action of Sulphur dioxide and Sulphuretted hydrogen whilst neither of them singly has any action. He developed a 'resonance' or 'vibration' theory of explaining geometrical inversion on the strength of this phenomenon. Whilst searching for further experimental confirmation of Skraup's work we have found that neither manganese dioxide nor sulphur dioxide inverts maleic acid but when sulphur dioxide is passed into a solution of maleic acid in which manganese dioxide is suspended it is converted into fumaric acid, the yield being greater than in Skraup's experiment. The conditions under which the inversion takes place have been studied in detail.

136. Combustion of charcoal in oxygen, nitrous oxide and nitric oxide.

M. S. SHAH.

The combustion of purified sugar charcoal in oxygen, nitrous oxide and nitric oxide has been studied both by a static and a dynamic method.

The qualitative and quantitative investigation of these reactions show that the probable mechanism in the process of combustion before CO and CO<sub>2</sub> are evolved, is (A) in O<sub>2</sub> and N<sub>2</sub>O and (B) in NO.





The union between carbon and oxygen is purely chemical as fixation of oxygen also occurs as a result of chemical decomposition of  $\text{N}_2\text{O}$  and  $\text{NO}$ . This union is very feeble below  $-78^\circ\text{C}$ , moderately so between  $-78^\circ\text{C}$  and  $50^\circ\text{C}$  and increases in strength above  $50^\circ\text{C}$  when the temperature is raised.

The spectroscopic examination revealed that the flame combustion of charcoal in  $\text{O}_2$  and  $\text{N}_2\text{O}$  is due to the oxidation of  $\text{CO}$  in the gaseous phase by  $\text{N}_2\text{O}$  or  $\text{O}_2$ . No flame is observed in the reaction with  $\text{NO}$ ; this is due to the oxidation of  $\text{CO}$  by  $\text{NO}$  at the time of its formation in the pores of charcoal whereby the possibility of a gaseous reaction is obviated.

The view that  $\text{CO}_2$  is the first product of combustion and that  $\text{CO}$  is obtained on subsequent reduction is found to be untenable. It is highly probable from the difference in the behaviour of  $\text{N}_2\text{O}$  and  $\text{NO}$  towards charcoal and from the proportion of  $\text{CO}$  evolved in Oxygen experiments, that  $\text{CO}$  is the primary product and  $\text{CO}_2$  is obtained along with it due to subsequent oxidation of  $\text{CO}$  by the fixed or the adsorbed layer of oxygen in charcoal.

The results throw some light on the mechanism of adsorption. The process consists of surface condensation alone in the cases of  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{N}_2$ , and of both surface condensation and chemical reaction in the cases of  $\text{O}_2$  and  $\text{NO}$  at  $0^\circ\text{C}$ .

Similar attempts are at present made to elucidate the mechanism of the combustion of sulphur in these gases.

### 137. Examination of the active principle of Indian henna.

SYED BASHIR ALI.

Water extract is treated with lead acetate, lead removed by sulphuretted hydrogen, and the active principle extracted by means of Benzene.

- (a) It is quite a pure product for it gave a constant M.P.
- (b) It is easily oxidisable, the colour changes to dark red even on exposure to air. The oxidised product can be easily reduced by Zinc and Hydrochloric acid.
- (c) The formula found differs from those given by previous workers.

### 138. Melting points and saturation points of sodium thio-sulphate and sodium sulphate by the conductivity method.

CHETAN ANAND and HAR GOBIND.

The conductivity method has been used by different observers for determining the transition points of salts in aqueous and non-aqueous solutions. Resistance of solutions of the salts are measured at different temperatures and the resistance-temperature graphs on being plotted indicate abrupt changes at the transition points. The method was applied to sodium thiosulphate and sodium sulphate in aqueous solutions. These salts have a comparatively low melting point, are highly soluble in water, and can easily be obtained in the supersaturated condition. Therefore if transition occurs at the melting point in the solutions, it will be indicated on the graphs. Resistances of various solutions were measured over a range of temperatures which went above and below the melting point of the salts and the saturation points of the solutions. The resistance-temperature graphs for Sodium Sulphate show at its melting point ( $33^\circ\text{C}$ ) a clear transition point for all concentrations and also a second transition point at the saturation point which varies with the strength of the solution. The graphs for Sodium Thiosulphate give two transition points. The melting point varies between  $45^\circ\text{C}$  and  $50^\circ\text{C}$  with different concentrations.



## 139. Inversion of cane sugar by tartaric acid.

DHARM SINGH, KISHEN LAL and CHETAN ANAND.

The action continues for several days at ordinary temperatures and can be studied conveniently by a polarimeter. Mixtures of cane sugar and tartaric acid were prepared in varying proportions, and their activities measured after equal intervals of time. The results are graphically shown. The rate of inversion is comparatively slow when the ratio of the acid to sugar is the lowest. The curves obtained are very striking. The activity of tartaric acid, as would be expected, plays no part in the reaction. The graphs for the more active and the less active varieties run exactly parallel to each other. The sugar is completely inverted after boiling; the activity of the acid appears only as an additive property.

Observations on different concentrations of sugar with a constant quantity of acid indicate that the rates of inversion follow a straight line law; for a given concentration of sugar acted on by different quantities of acid, the rates of inversion do not show a simple relation.

## 140. The condensations of esters with Resorcin, Di-methylaniline and Diethyl-m-aminophenol.

R. N. SEN and ASHUTOSH MUKHERJEE.

Previously Resorcinol and Pyrogallol were condensed with methyl Salicylate to produce compounds of the Benzein series. (Sen and Guha Sarkar Journal Ind. Chem. Society Vol. I issue No. 2 pp. 157.)

In elaboration of that reaction, Benzoic ester has now been condensed with resorcinol by heating to  $180^{\circ}\text{C}$  in the presence of  $\text{ZnCl}_2$ . Resorcinol-Benzein is produced with the intermediate formation of 2-4 Dioxo Benzophenone which has also been isolated. The following other esters have also been successfully condensed with resorcin:—O-nitro-, O-amino-, and p-amino-, Benzoic esters; naphthoic ester; oleic and stearic esters; and the effect on the reactivity and the yield as also upon the colour and fluorescence of the products has been studied. The compounds dye wool and silk yellow to brown shades while the Bromo derivatives dye red shades.

The natural oils, being analogous to esters, have been similarly condensed with resorcin. Coconut oil, olive oil and castor oil have been made to yield dyes in this way, producing yellow to brown shades on wool and silk, bright red shades being produced by the Bromo compounds. Benzoic ester, O-hydroxy, O-amino and p-amino- Benzoic esters and naphthoic ester have also been condensed with Di-methylaniline in the presence of  $\text{ZnCl}_2$  and  $\text{POCl}_3$  to give malachite green and dyes of the malachite green series. The dye base is formed directly and so the oxidation of the leucobase is not necessary.

Rhodamines have been obtained by the condensation of Di-ethyl-m-aminophenol with Benzoic ester, anthranilic ester and stearic ester in the presence of  $\text{ZnCl}_2$ . Incidentally in the case of Benzoic ester an acridine dye, Di-oxyphenylacridine, has been obtained with HCl as condensing agent.

141. Condensation of levulinic acid ( $\overset{\delta}{\text{CH}_3} \overset{\beta}{\text{CO}} \overset{\alpha}{\text{CH}_2} \text{CH}_2 \text{COOH}$ ) with aldehydes ( $-\text{CHO}$ ).

R. N. SEN and BIRESH CHANDRA ROY.

Levulinic acid was previously condensed with benzaldehyde, furfuraldehyde, and a few substituted benzaldehydes by several investigators, (Erdmann 1886, Ber. 18,3441-43, Annalen 258,129-33; Erlenmeyer-Ber 23,74-76; Ludwig and Kehrler-Ber 24,276-78; Erdmann and Kehrler-Ber 26,345; Meigash-Monatsch 26,2675-77; Borsche-Ber 1915, 48,842-49).



In the present investigation the acid has further been condensed with various aldehydes (Benzaldehyde, monohydroxy benzaldehyde, resorcylic aldehyde, beta-naphthyl aldehyde, nitro-benzaldehyde, furfuraldehyde, citral, piperonal, anisaldehyde, vanilin, glucose) with interesting results. Alpha-condensations taking place in presence of acetic anhydride, beta-condensations taking place with dry HCl gas whereas the condensation takes place at the delta-position when dilute caustic soda solution is the condensing agent.

Alpha-beta and delta-beta condensations (dibenzylidene compounds) have also been effected in many cases carrying out the reactions successively with different condensing agents.

The condensation products have afforded further opportunities of studying the possibilities of the formation of interesting ring compounds by the action of suitable dehydrating agents.

With acetic anhydride as the condensing agent the beta-condensation products have in all cases yielded naphthalene derivatives; whereas the delta products under similar circumstances have yielded a new type of cyclic compounds which may be looked upon as being formed by the coalescence of an eight membered ring with a benzene nucleus.

By condensing m-nitro and m-hydroxy benzaldehydes with levulinic acid in presence of dry HCl gas, naphthalene derivatives are formed at once beta-condensations and ring formation taking place simultaneously.

It is remarkable however that in the case of piperonal as well as vanilin naphthalene derivatives are also obtained at once.

In the case of O-hydroxy compounds as well as with several delta-condensation products seven membered and five membered lactones have been obtained, the former exhibiting marked dyeing properties.

#### 142. Studies in azo-triphenylmethane and azopyronine dyes.

R. N. SEN *and* B. C. GHOSH.

#### 143. On the reactivity of ortho-diketonic groups placed between two nitrogen atoms.

ANUKUL CHANDRA SIRCAR *and* PRAN KUMAR DE.

In attempting to prepare azine derivatives by the condensation of Ortho-diamines with diphenyl-thioparabanic acid and similar other bodies, it has been found that the ortho-diketo groups when placed between two nitrogen atoms behave quite differently towards ortho-diamines than when placed between two carbon atoms,—as in phenanthraquinone. Thus by the condensation of ortho-phenylene diamine with diphenyl-thio-parabanic acid no azine could be obtained, but phenylene-oxamide, phenylene-thiourea and aniline were isolated from the reaction mixture. Dinitro-diphenyl-thio parabanic acid and diphenyl parabanic acid behave exactly in the same way. An explanation of the mechanism of the reaction is given

#### 144. Equilibrium diagram of the system lead-arsenic.

MOHAMMAD OMAR FARUQ.

Arsenic alloys with Lead in all proportions. The diagram was studied up to 60% Arsenic. Lead does not dissolve any Arsenic at its melting point but at higher temperatures two layers are formed. The lower layer being Lead containing a small quantity of Arsenic in it and the upper layer of Arsenic with small quantity of Lead dissolved in it.



# INDIAN SCIENCE CONGRESS.

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ABSTRACTS OF PAPERS.

Section of Zoology.

*President :—Dr. B. Sundara Raj, M.A., Ph.D.*

CALCUTTA.  
ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Zoology.

### Abstracts.

1. Observation on the incubation of the eggs and the development of the embryo of *Calotes versicolor* Boulenger.

J. J. ASANA, Ahmedabad.

The writer has been making observations for the last three years on the egg-laying habits and the eggs of *Calotes* both amidst natural conditions in the field and in the laboratory, with a view to obtaining closely graded embryonic stages for the study of the germ cell descent and embryonic development.

The eggs are laid in moist sandy earth, about 5 to 7 inches deep, in clutches of 13 to 20 eggs, which are separate and not glued together. The egg-laying period commences about the middle or third week of June, and lasts till about the end of August or first week of September. In the majority of cases the eggs were collected soon after laid, after a period varying from 1 to 48 hours and kept in moist earth at room-temperature exposed to ordinary diffuse sunlight, the earth being kept moist by sprinkling water on it at intervals. Two gravid females kept in confinement in the laboratory for about 8 to 10 days had their abdomen cut open, almost fully matured, shelled eggs were taken out from the oviducts and kept in moist earth under laboratory conditions for incubation. They were found to behave as ordinary naturally laid eggs. Successive stages of the developing embryo were collected and carefully fixed and preserved.

The fully laid egg is ovoid in shape, one end slightly pointed and is about 10 to 11 mm. in longer diameter and about 4 to 5 mm. in its shorter diameter. After about 24 hours' growth it has increased about 2 mm. in both directions. It shows very rapid growth from the 4th to the 5th day onwards till about the 16th to 18th day of its incubation, measuring roughly 2 c.m. and 1.3 c.m. in its longer and shorter diameter respectively, just before the young lizard is hatched.

Under laboratory conditions the young ones came out of the eggs after a period of development lasting over 43 to 46 days from the time of laying.

2. A preliminary note on the spermatogenesis of *Poecilocera picta* Fabr., Sub-family Pyrgomorphinae, Orthoptera.

J. J. ASANA, Ahmedabad.

Both male and female specimens of *P. picta* are found in fairly large numbers on *Calotropis* and on *Euphorbia* hedge from the middle of June to late in November. They are not difficult to keep and though no attempt has been made to breed them under laboratory conditions, they freely copulate and females were found laying eggs in the cage. Nymphs in the late instar stages have been collected from the field late in June and the beginning of July since 1925. Males are comparatively smaller in size than the females. Gonads are easy to dissect and could be passed into fixatives in less than half a minute. Several fixatives used in modern cytological technique both for the study of the nucleus and the cytoplas-



mic inclusions were attempted. Flemming with and without acetic, dilute Bouin, and Da Fano have been found to be more successful so far. Original method of Mann Kopsch, Ludford's modification and Kotatchev have been given a few trials but with little success.

The male germ cells are of fairly large size and offer an exceptional opportunity for a study of the prophases on the lines indicated by Dr. McClung in his recent paper on Synapsis in *Mecostethus* in the Journ. of Morph. and Physio., Vol. 43, No. 2. In the auxocytes the "diatene," "peritene," "phanerosome," "cryptosome" stages in synapsis, preceding diakinesis could be clearly made out. At the completion of diakinesis, nine bivalents and one large unpaired, slightly bent, rod shaped, accessory chromosome are seen on the equatorial plate ready for the reduction division. Polar views of the late anaphase in the reducing division show nine V-shaped chromosomes at one pole and nine V-shaped chromosomes with the single rod shaped accessory chromosome at the other pole. The succeeding division is equational and quickly follows the almost transitory telophase of the preceding reduction division.

The bivalents show distinctive chromosome sizes and shapes, the seriation being one large, two slightly smaller, five intermediate and one small bivalents and one unpaired, univalent sex-chromosome. The accessory or sex-chromosome shows a very characteristic behaviour, varying its size and shape, throughout the early auxocyte prophases.

The process of spermatid formation is of comparatively long duration, and from the study of the "nebenkern" one may infer that here one witnesses spermeteosis of a primitive nature.

### 3. On the anatomy of the stomach in *Paludomus tanjorensis*.

R. V. SESHAIYA., Tirupati.

1. The stomach of *Paludomus* is of interest due to the possession of a crystalline style. 2. The crystalline style is lodged in an anterior chamber of the stomach. 3. The style sac is separated from the intestine but the opening of the style sac into the stomach communicates by a slit with the portion of the stomach into which the intestine opens. 4. This condition is a transition very nearly approaching the one in which there is perfect separation between the style sac and the intestine. 5. A ciliated groove is present in the style sac and it is the abbreviated continuation of the communication between the opening of the style sac and the intestinal region of the stomach. 6. The style sac epithelium has the usual structure. 7. The style is probably secreted by the ciliated groove and is held at its anterior end within the circular termination of the ciliated groove. 8. A gastric shield is present and cuticle is developed on the epithelial walls in the region of gastric shield. 9. In connection with the gastric shield special folds of the ventral wall of the stomach are developed. 10. Glandular folds are present.

### 4. Ceratium in plankton off Calicut.

S. T. MOSES.

Ceratium, with other Dinoflagellates, Flagellates and Diatoms, the food of the oil-sardine, a plankton feeder. Analysis showing the relative abundance or otherwise of Ceratium during 6 years from November, 1921. The Calicut species (1) *Euceratium tripos*, (2) *E. breve*, (3) *E. trichoceras*, (4) *E. massiliense*, (5) *E. vultur*, (6) *Biceratium lineatum*, (7) *B. furcata typica*, (8) *B. f. engramma*, and (9) *Triceratium fusus*. The Phosphorescent species.



5. On the behaviour of Golgi apparatus in the oogenesis of *Calotes Versicolor* Boulenger.

S. K. DUTTA and J. J. ASANA, Ahmedabad.

This paper attempts only to give a preliminary account of certain cytoplasmic inclusions in the oogenesis of the common Indian lizard, *Calotes versicolor*.

The ovaries of *Calotes versicolor* were fixed by various methods of modern cytological technique, of which only two, DaFano's Cobalt Nitrate method and Ludford's latest modification of the Osmic method, gave us the desired results.

In the young oocyte the Golgi bodies appear as a complex dense mass in the usual juxtannuclear position and consist mainly of granules.

In the later stages, the Golgi bodies become scattered in the cytoplasm and gradually become ultramicroscopic in the medullary region. Comparatively bigger Golgi spherules arrange themselves in a ring as a cortical layer. Subsequently, with the development of the egg they are broken up and lost to view in the general cytoplasm. At a particular stage of development, the follicular epithelium becomes very active and a large number of Golgi spherules appear to be extruded from the epithelial cells into the egg. They pass through the zona radiata and settle down in the extreme peripheral region of the egg where they are indistinguishable from the original Golgi spherules of the developing oocyte.

The Golgi bodies either directly or indirectly contribute to the formation of yolk.

The mitochondria which are visible in Ludford slides stained by Chamy-kull technique, are probably responsible for the formation of true yolk.

6. On the habits of *Stegodyphus sarasinorum* Karsch.

P. M. SOMASUNDARAN, Bangalore.

Some glimpses into the social life of this gregarious spider, the constitution of a community, nest and web building, capture of prey and method of feeding, relation of the sexes, eggs and cocoons, parental care.

7. Note on the function of the mitochondria in some soil protozoa.

H. S. MADHAVA RAO, Bangalore.

Various species of protozoa occurring in soils have been isolated and grown in pure culture. Organisms at different stages of the life history were obtained and stained by means of the sodium salt of diethyl safranine monocarboxylic acid which stains the mitochondria only. The latter appear to be true cytoplasmic bodies and digestive in function, increasing in number by binary fission.

8. Preliminary note on the protozoa from some Mysore soils.

H. S. MADHAVA RAO and ROLAND V. NORRIS, Bangalore.

Typical soils of the Mysore area have been examined for their protozoal content and a study of the organisms isolated has been made. Three species apparently not previously described have been noted.



## 9. Two acanthocephalous worms from indian fishes.

S. C. VERMA and M. N. DATTA, Allahabad.

The senior author, in the course of his investigation on the Trematode and Cestode parasites of indian food fishes came across some thin, cylindrical, elongated Acanthocephala in the pyloric caeca and small intestine of a species of *Ophiocephalus* at Mainpuri, U.P., in the summer of 1926; more specimens were subsequently collected at Allahabad also. The worm is a new species of the genus *Quadrigrigous* Van Cleave, 1923, and is described in this paper.

Numerous specimens of another species were obtained by the same author in June, 1927, and later by the second author from a species of *Macrones* at Calcutta. This species belongs to the genus *Neoechinorhynchus* and has got no hooks on the anterior part of the body. There are three rows of six hooks each on the proboscis. Description of the cement gland, testes, proboscis sheath, and body wall are given.

## 10. Some tetraphyllid Cestodes from indian Fishes.

S. C. VERMA, Allahabad.

*Introduction.* Four new species of tetraphyllid cestodes are fully described. One of these belongs to the genus *Acanthobothrium* of the family Onchobothriidae. The other three are referable to the family Ichthyotæniidae, one falling under the genus *Ichthyotaenia*, and two under *Gangesia*.

The species, "*Gangesia bengalensis*," described by Southwell (1913) as "*Ophryocotyle bengalensis*" and more fully by Woodland (1924) as *Gangesia wallago* is reconsidered as the latter description is in several respects misleading owing to confusion by the author of two distinct forms occurring in the same host into one.

Mention is also made of an immature worm of the family Phyllobothriidae from a fresh water siluroid, the systematic position of which is still under inquiry, and a new host is recorded of the monozoan cestode *Amphilina paragonopora*.

*Acanthobothrium semnovesiculum* nov. sp. This species was obtained from the common skate *Trygon Sephen Day-Hypolophus Sephen* Chandler caught from the rivers Ganges and Jumna at Allahabad. It has a conspicuous characteristic vesicula seminalis which, apart from other features, at once marks it out from the known species of the genus. In addition to an account of its anatomy, affinities and diagnostic features, a key to the species of the genus (after Southwell) is given modified to include the new form.

*Ichthyotaenia vitellaris* nov. spec. This is a large tapeworm occurring in the intestine of *Bagarius yarrellii* Sykes, containing about 700 segments. It is characterised by a prominent cap-like apical organ, and the peculiar L-shaped vitellaria like that of *Proteocephalus perplexus* La Rue, 1914. Some interesting abnormalities are noted in connection with the ovary and the related ducts. The systematic position of the new species is indicated and its diagnosis given.

*Gangesia pseudotropii* nov. spec. This interesting type of cestode remarkable in more ways than one, parasitises *Pseudotropius garua* Day. It has a rostellum bearing at its top an apical organ, fringed with a beautiful crown of large hooks, well adapted to serve as an efficient boring organ. This armed rostellum is an essential characteristic of the genus *Gangesia*. But its two-field distribution of testes with a tendency to coalesce anteriorly is a common *Crepidobothrium* (*Ophiotaenia*) feature. Adopting the definition of the Woodlandian genus *Gangesia* as modified by Meggitt (1927) to include the two characters mentioned above the type fits in within this genus. The addition of a sentence in the definition of the genus, relating to the occurrence of spines on the



body of these worms, is suggested. Another remarkable feature of this parasite—the development of some embryos, at least, into a cysticercus or bladderworm stage while still within the uterus of detached ripe and gravid proglottids found free living in the hind gut of the host—is noticed.

*Gangesia agrænsis* nov. sp. This species is met with in the intestine of *Wallago attu* (in various parts of the province of Agra) along with specimens of *Gangesia bengalensis*. It differs from the latter by its smaller size, by the shape, size, number and arrangement of the rostellar hooks and by the much larger number of testes in each segment.

*Gangesia bengalensis* Southwell 1913. This species is reconsidered and the description given of it by Woodland 1924, is modified in some respects.

Diagnoses of the above three species are furnished and the key of the genus *Gangesia*, drawn up by Meggitt (1927) is revised to include the forms above described.

## 11. On cytoplasmic inclusions in the oogenesis of certain molluscs.

D. R. BHATTACHARYA and C. B. MATHUR, Allahabad.

In very young oocytes, the Golgi apparatus is, as usual, juxtannuclear, and consists of a number of circular and crescent-shaped bodies imbedded, as it were, in the idiosome. These ring-like and crescent-shaped bodies have a sharp chromophilic rim and a central chromophobic substance. The Golgi bodies in the animals examined appear to give rise to fatty yolk. The mitochondria contribute towards the formation of true yolk spheres both directly and indirectly. The nucleolar extrusions do not apparently take any part in yolk formation.

## 12. The reproductive processes of *Pila globosa* Swainson.

K. N. BAHL, Lucknow.

No observations have hitherto been published regarding the reproductive processes of any Ampullarid. Baini Prashad in his monograph on *Pila globosa* says that he has not been able to observe these phenomena.

Since *Pila* (*Ampullaria*) is studied as a type of the Gastropoda in almost all the Indian Universities, it is necessary to have as complete a knowledge as possible of this form and I therefore undertook to study its breeding habits. The following is a summary of my observations:—

- (1) After a prolonged period of æstivation during dry months, *Pila* comes out at the onset of the rains and begins breeding forthwith.
- (2) Copulation takes place in water or on the ground at the edge of a pond. It lasts for about three hours or more.
- (3) The penis being a structure independent of the male generative aperture, the genital gland acts as a miniature second penis and effects the transference of the spermatic fluid from the male pore to the base of the penis proper.
- (4) Both the penis-sheath and the penis are inserted into the mantle-cavity of the female and the free end of the penis is inserted into the vagina. Impregnation is internal.
- (5) Oviposition takes place within a day or two after copulation and the foot acts as a very efficient ovipositor.
- (6) Eggs are laid on the ground in small hollows in large masses. Each egg-mass usually contains 200 to 300 eggs but I have come across some very large egg-masses containing 700 to 800 eggs.
- (7) Each egg consists of a shell, a double shellmembrane, a thick



layer of opaque solid albumen, and a core of fluid albumen in which the embryo floats.

13. Distribution of some freshwater species of the families Belonidae and Hemirhamphidae.

B. PRASHAD, Calcutta.

The distribution of two species of the families Belonidae and Hemirhamphidae is discussed in detail, and the question of the origin of these freshwater species in distinct river-systems is considered. It is suggested that this occurrence of the same species in these disconnected water-systems can be accounted for by assuming that these fishes had adapted themselves independently in these areas. Owing to the absence of the species in the intervening seas it is further suggested that they probably originated from marine ancestors independently in the different areas.

14. Studies on the Viviparidae.

B. PRASHAD, Calcutta.

Amongst the freshwater Gastropods the members of the family Viviparidae are of special interest in that they have a very peculiar and discontinuous distribution almost all over the World. Both the recent and fossil members of the family are discussed in detail and a sketch-map illustrating the distribution of the recent members of this family is exhibited. The methods of dispersal, the question of the origin and the relationships of the family are discussed in detail and it is concluded that the family probably had a polyphyletic origin.

15. A note on the aquatic molluscs of the Shan States, Burma.

H. SRINIVASA RAO, Calcutta.

A brief general account is given of the freshwater molluscs occurring in the Shan States with special reference to the types of environment common in the region. The geographical distribution of the Shan species, and their affinities to the mollusc fauna of adjacent territories are discussed.

16. On the infiltration of Golgi bodies from the follicular epithelium to the egg.

D. R. BHATTACHARYA, R. S. DAS and S. K. DUTTA,  
Allahabad.

Bhattacharya in the tortoise and Brambell in the fowl, have already described the infiltration of either minute or large Golgi elements from the follicular epithelial cells to the periphery of the egg. These bodies either filter through small canalicular spaces in the Zona radiata or are extruded as comparatively larger lumps from the follicular cells to the zona radiata and from thence to the extreme periphery of the egg. The latter method of the passage of Golgi bodies has been observed by the present authors to be taking place also in the toad, pigeons and several other birds, *Calotes* and various other reptiles. The process of infiltration or extrusion is confined to a particular stage in the development of the oocyte. The structure and possible functions of these Golgi bodies have been discussed.



17. A preliminary account of the cytoplasmic inclusions in the oogenesis of *Columba intermedia*.

RAM SARAN DAS, Allahabad.

This paper purports to give only a preliminary account of the oogenesis of *Columba intermedia* from the point of view of cytoplasmic inclusions.

The usual cytological fixatives were used with this difference that "the cold method" advocated by Parat was largely employed. This gave us very satisfactory results.

The Golgi bodies acquire the usual juxtannuclear position in the early stages of development at one pole of the nucleus. Later on they take a perinuclear position and are soon replaced by a fatty yolk layer.

The Golgi bodies of the cells of the egg membranes at a particular stage seem to acquire unusual activity and travel through the zona radiata into the cortex of the egg. Here they arrange themselves into a dust-like cortical layer of extremely minute granules. What further part they play in the development of the egg is uncertain.

Mitochondria in the early stages form a cap-like dense cloud over one pole of the nucleus. Subsequently they become distributed throughout the cytoplasm. In older oocytes a peripheral zone of mitochondria becomes noticeable.

In very young oocytes fat droplets or yolk become a characteristic feature of the developing oocytes. The perinuclear layer of the Golgi bodies is soon replaced by the fatty yolk which appears to have started formation even when the Golgi apparatus lies in the region which is generally designated as the yolk-nucleus of Balbiani or the dense protoplasmic area adjacent to the nucleus. There seems little doubt that the Golgi bodies become directly or indirectly converted into fatty yolk or what others call fatty vacuoles or droplets.

True yolk appears to be formed by the direct metamorphosis of mitochondria inside a vacuole. Neither nucleus nor cytoplasm appears to take a direct part in the formation of the true yolk bodies.

18. Cytoplasmic inclusions in the oogenesis<sup>o</sup> of *Bufo melanostictus*, *Rana tigrina* and *Rhacophorus Fergusonii*.

DHARAM NARAIN, Allahabad.

The Golgi bodies are noticed in very young oocytes in the usual juxtannuclear position at one pole of the nucleus. Later they begin to spread out and take a perinuclear position from where they disperse in the general cytoplasm and form fatty yolk.

In older oocytes a definite layer of dust-like golgi bodies is found in the cortical region near the zona radiata. There is evidence to believe that these bodies migrate from the follicular epithelium.

In the early stages, the mitochondria form a cap-like dense cloud over one pole of the nucleus. Later they disperse and become distributed throughout the cytoplasm. Only spherical mitochondria could be detected.

True yolk is probably formed by the metamorphosis of mitochondria. Neither nucleus nor cytoplasm appears to take a direct part in the formation of true yolk-bodies.

Very minute spherical fragments are extruded from the nucleus on all sides. They lose their colourability and are lost in the general cytoplasm.



## 19. Report on a collection of ants in the Indian Museum.

DURGADAS MUKERJEE, Calcutta.

The report is based upon a collection of ants consisting of 40 species representing different sub-families. The majority of species recorded here come from the Himalayas, a few from the Palni Hills, South India, Seistan, and the rest from Calcutta. The report includes descriptions of five new species and brief notes on the habits of ants common in Calcutta and shows the altitudinal distribution of ants along the Himalayas. The collection was received through the courtesy of Lt. Col. Seymour Sewell.

## 20. Notes on habits, structure and life history of an Indian Gordius worm.

DURGADAS MUKERJEE, Calcutta.

Several male and female Gordius worms were found wriggling on earth covered with rain water. The worms appear in the rainy season just after a heavy shower. They swim freely in water but generally intertwine with one another to form a tangled mass. They were kept in captivity and lived for a month. The captive females laid small strings of eggs. The eggs hatched after a month into minute larvae provided with an intestine and an introvert. The introvert contains minute spines at the base and its terminal end. The larvae were kept alive in water for a month and as the asexual stage is passed in the parasitic condition, an attempt was made to infect different animals with the larvae. The adult males have their posterior ends bifid while the females are without any bifurcations or lobes at their posterior ends.

## 21. Observation on the course of the facial vein and the formation of the external jugular vein in common frogs and toads of Bengal.

J. L. BHADURI, Calcutta.

The facial vein in frog, according to Gaupp, continues beyond the head as the cutaneous vein. But in *Bufo melanostictus*, the present author observes that the facial vein instead of continuing as the cutaneous vein, curves round the angle of the jaw to open into the internal mandibular vein. He further notes that in *Rana tigrina* the facial vein, while continuing posteriorly as the cutaneous vein, sends off a branch round the angle of the jaw to open into the internal mandibular vein as in *Bufo*. In text books it is stated that the internal mandibular and the lingual veins unite to form the external jugular vein. But as seen in the present instances a common trunk formed by the union of mandibular and facial veins, unites with the lingual vein to form the external jugular vein. To distinguish this common trunk from the posterior portion of the mandibular vein the present author holds that the trunk should conveniently be called facio-mandibular vein.

## 22. Venous abnormalities in common frogs and toads of Bengal.

J. L. BHADURI, Calcutta.

The cases of abnormalities in the vascular system of frogs and toads dealt with in this paper have not yet been recorded in India. The author describes the following types of abnormalities which he came across during class demonstration

- (i) A peculiar venous ring girdling the carotid arch in a female toad.



The formation of the ring was due to the bifurcations of the right lingual vein and their union with the right external jugular vein.

(ii) Presence of several venous peculiarities in a single female toad.

- (a) persistence of the left posterior cardinal vein.
- (b) unusual thickness of the anterior abdominal vein.
- (c) absence of post-caval vein,—two very large hepatic veins opening directly into the sinus venosus.
- (d) a peculiar vein arising from the dorsal part of the oesophagus opening into the isthmus of the liver.

(iii) Truncated anterior abdominal vein in a female frog. The abdominal vein instead of opening into the liver terminates in a knob in the region of the liver. Nine cases of abnormalities in the anterior abdominal vein have been reported,—but no such knobbed condition has yet been recorded.

### 23. A case of hermaphroditism in *Rana tigrina*.

J. L. BHADURI, Calcutta.

This frog externally exhibited the characteristic features of a male, while internally it showed a pair of thin convoluted oviducts and two small testes of equal size. Ovaries were apparently absent.

### 24. Note on a double Chick embryo.

J. L. BHADURI, Calcutta.

A pair of chick embryos was found lying with their cephalic ends touching each other and their caudal ends diverging. Both the embryos showed normal features having their head regions divided into fore-brain, mid-brain and hind-brain, with well-developed optic vesicles, prominent notochord and primitive streak. The head regions of both were covered by a common proamniotic fold. Their general features were more or less similar but the numbers of segments in the two were different. The embryo on the left hand side contained 16 segments and the right 18. The occurrence of two such embryos in a single incubated egg at this stage is peculiar.

### 25. On the bionomics and structure of a new Trematode *Ommatobrephus lobatum* n. sp. from *Zamenis mucosus*.

H. R. MEHRA, Allahabad.

Hitherto only one species of the genus *Ommatobrephus* has been described by Nicoll from *Uromastix acanthinurus*. The new species is a common parasite attached firmly by its huge ventral sucker to the walls of the rectum of the common rat snake.

A full account of the species and a discussion of the systematic position of the genus is given. The most important features are the unusual position of the testes near the hind end of the body and the precocious development of the miracidia. The latter were observed to come out of the genital opening and carefully studied. The excretory system is aberrant from that of the family.

Two specimens belonging to a new variety were obtained from the rectum of a cobra.



26. On a new genus *Spinometra* belonging to the family Lepodermatidae from *Kachuga dogonga*.

H. R. MEHRA, Allahabad.

The parasites are obtained from the small intestine and possess a very long protrusible cirrus. The genus does not show the phenomenon of amphitypy. Cirrus pouch is very large and contains a much coiled vesiculum seminalis. Genital pore is situated close in front of the ventral sucker to the left side. The oral sucker is very small about one third in size of the ventral sucker.

The genus no doubt belongs to the sub-family Cymatocarpinae Baer, but it differs remarkably from all the genera in practically all the features of its anatomy which are described in detail.

27. A note on the life history of *Chonocephalus depressus* de Meiz—Fam. Phoridae (Diptera).

Rao Sahib Y. RAMACHANDRA RAO, Coimbatore

*Chonocephalus depressus* de Meiz was described by Professor J. C. H. de Meizere of Netherlands Museum, Amsterdam in 1912 from a female specimen from Medan (Sumatra). At Coimbatore this Phorid was found breeding in rotting fruit pulp in cages at the Insectary in 1913 and its life history was followed during the following year and notes taken on its various stages. While the females are wingless and resemble nymphs of Psocids, the males possess wings showing the typical neuration of Phorids. The males were observed to fly about carrying the wingless females in copulation. A description of the male form of *Ch. depressus* is given for the first time. The maggot is peculiar in possessing a retractile rat-tail like appendage at the hind extremity.

28. The life history of *Cyphocera varia*—a Tachinid parasite on *Spodoptera mauritia*.

S. RAMACHANDRAN, Madras.

This paper gives a detailed account of the life-history and habits of *Cyphocera varia*, an important Tachinid Fly parasitic on Caterpillars of *Spodoptera mauritia*. The fly has the very interesting habit of depositing its maggots on the trails of its host. These maggots wait at the spots, till one of the caterpillars happens to pass by them, when they attach themselves to it, bore into its body and feed there till pupation. The parasite with its highly specialised habits of reproduction is undoubtedly a great factor in controlling the recurrence of the pest in certain localities, for instances are on record where nearly 90% of the caterpillars and pupae collected had been parasitised by this fly.

Attempts are made in the paper to describe the development of the buccopharyngeal armature, and the posterior and anterior spiracles in the different stages of the maggot. Various other points connected with the life history of the fly such as the habits of the fly, its longevity, methods of larviposition, reproductive capacity, power of endurance of the maggots etc. have been worked out.

29. A short note on a novel pest of tobacco—*Stibaropus tabulatus* Sch.

P. N. KRISHNA AYYAR.

*Stibaropus tabulatus* Schiodte is a Pentatomid bug which was observed to have the singular habit of attacking the roots of tobacco in a village in Coimbatore District. Though the insect was noted only in



one garden, the extent of damage done was not inconsiderable. The curious habits of this Pentatomid are described and an account of its life history given as far as could be worked out. Application of crude oil emulsion in varying proportions was tried and promising results were obtained by its application at a certain strength.

### 30. Hermaphrodite organs of indian leech.

M. L. BHATIA, Lucknow.

#### Male organs:—

There are eleven pairs of testes segmentally arranged from the 12th to the 22nd somites connected with the vasa deferentia of the corresponding side. In front of the first pair of the testes *i.e.* in segment 11 the vasa deferentia continue their normal course, but in segment ten they increase in width and form complex coils, the epididymis. From the inner side of each a short ejaculatory duct opens at the base of the penis which is an eversible globular organ lying in segment tenth.

#### Female organs:—

The female organs lie entirely in the eleventh segment. The ovaries are a pair of minute filamentous bodies enclosed in small sacs lying close to the mid-ventral line and continued into short oviducts, the left oviduct passing under the nerve cord. The vagina is an elongated sac like structure, expanded at the base but narrow at its distal end which opens to the exterior between the 2nd and 3rd annuli of segment eleven *i.e.* between rings 35 and 36.

The variations from the condition in *Hirudo medicinalis* are detailed in the paper.

### 31. Copulation in the common indian leech.

M. L. BHATIA, Lucknow.

Leeches are hermaphrodite, each individual possessing two complete systems of generative organs one subservient to impregnation, the other to the production of ova. These animals, however, are not self impregnating and the union of the two individuals is essential for fertilization.

Two worms become attached to each other in a head to tail position in such a way that the annuli 30-31 of one, where the male aperture is situated, are apposed to annuli 35-36 of the other (the position of female aperture) and vice versa.

In this condition there is mutual exchange of seminal fluid which issues from the male aperture and is conveyed to the vagina by a tubular and eversible penis. After the exchange of the seminal fluid, the two worms separate.

### 32. Cocoon formation by *Hirudinaria granulosa*.

M. L. BHATIA, Lucknow.

The area of the body between 30th and 26th annuli is concerned in the formation of the cocoon. This portion of the animal may be called the clitellar region, though a permanent clitellum as we find it in earth-worms is never present. During the cocoon formation a white frothy girdle appears round these annuli, no doubt formed from the secretion of the epidermal glands in that region. The ova are ejected through the female aperture and the animal slowly withdraws its head through the froth by the rhythmic contractions of the body. When the head is completely withdrawn, the openings at the anterior and posterior ends of the cocoon soon close up. The process of cocoon laying lasts for about five to six hours. In about 24 hours the froth hardens, becomes brown and the cocoon assumes an oval shape, measuring 15 to 30 mm. in length.



The wall of the cocoon consists of an inner membranous layer and an outer spongy layer enclosing the air bubbles, which make the cocoon float in water.

33. Notes on the blood vascular system of *Uromastix hardwickii*.

M. L. BHATIA, Lucknow.

The external appearance of the heart of *Uromastix* is typically reptilian, consisting of a sinus venosus, two auricles, and a single ventricle. The valve guarding the auriculo-ventricular apertures is a membranous fold strengthened by fibrous tissue, giving the shape of two hoods and resemble very much a pocket valve. Arising from the ventricle are three aortic arches (pulmonary, left and right systemics). All these arches indicate a slight twist and cross each other at the point of their origin. Each of the three trunks is independently guarded by a pair of semilunar valves. Right systemic opens first into the ventricle at a place where the left systemic and the pulmonary are quite independent. The lumen of the left systemic becomes connected with the right systemic, then with the pulmonary ultimately opening into the ventricle. In the arterial system all the main branches supplying the alimentary canal arise separately from the dorsal aorta.

A detailed account of the venous and the arterial systems is also given.

34. Parasites of lac in Hyderabad and elsewhere.

S. MAHDIHASSAN, Hyderabad (Deccan).

A number of parasites have been reared from different varieties of lac. Some parasites are common while a few show specificity in the species they parasitise.

35. Some observations on the salt-water lakes near Calcutta.

B. CHOPRA, Calcutta.

A preliminary survey of the salt-water lakes near Calcutta was carried out in May, 1926. The lakes consist of vast stretches of shallow water connected with the Hugli, and have a bottom of soft ooze-like mud, in places more than two feet deep. The scarcity of species and a great abundance of individuals of each species is the most characteristic feature of the fauna of these lakes.

36. Preliminary observations on the Indawgyi Lake and its fauna.

B. CHOPRA, Calcutta.

The Indawgyi is the largest freshwater lake in Burma. In the dry season it is about 16 miles long and is over 6 miles broad near the south end. In places the lake is very deep, but near the north end it is shallow, the average depth there in the dry season being less than 12 feet. There are no floating islands in the lake, though large masses of weeds etc. agglutinated together are seen floating about at the north end. The lake is connected through the Indaw river with the Irrawady system.

The physical features of the lake are briefly compared with those of the Inle in S. Shan States and the Loktak in Assam.

The fauna of the lake is very rich, specially in fish and molluscs. Some species of fish grow to a very large size attaining a weight of well over 100 lbs. Another remarkable feature of the fish fauna is the presence in the lake of representatives of the families Tetraodontidae



and Syngnathidae. Fishes of these families are not so far known to occur in any other freshwater lake in India.

37. A note on fish-mortality in the Indawgyi Lake in Upper Burma.

B. CHOPRA and D. MUKERJI, Calcutta.

The physical features of the Indawgyi lake are briefly described in the foregoing paper. In the months of December and January every year very large numbers of fish die in the southern part of the lake for reasons so far unknown. The phenomenon of this mortality is briefly reported on in this paper.

38. On a curious mode of development of the suprabranchial labyrinthiform accessory air-breathing apparatus in the climbing-Perch.

B. K. DAS, Calcutta.

The air-breathing apparatus in the climbing-perch (*Anabas scandens*) consists of two parts, viz., an air-chamber situated on either side of the posterior region of the head in contact with the otic capsule, and a delicate shelly-labyrinthiform organ lodged inside the chamber. The air-chamber is derived from the dorsal outgrowth of the opercular cavity. It is lined internally by two or three layers of epithelial cells, richly provided with blood-capillaries,—mucous cells and vascular papillae (like those of *Clarias* and *Saccobranchus*) being absent; externally, however, the wall of the chamber is invested by a thin layer of connective tissue crossed over by a few muscular fibres. The air-chamber thus formed communicates both with the pharynx as well as the opercular cavity, and the passage of air is controlled by a valvular structure ('Tellerformiger Nebenorgan' of Wilh. Peters) derived from the dorsal surface of the first ceratobranchial.

Certain observations have been made on the development of the so-called labyrinthine organ.

The structure and the mode of development of this fish have also been compared with those of other Labyrinthicians.

39. Observations on the 'drowning experiences' of the indian fresh-water fishes of the Family Ophiocephalidae. (To be experimentally demonstrated.)

B. K. DAS, Calcutta.

The amphibious snake-headed fresh-water fishes or Ophiocephalids are generally inhabitants of foul water, and are known to come to the surface to breathe atmospheric air. At times they also come out of their natural element, "walk" and enjoy nocturnal peregrination, and are able to sustain life for at least 4 to 6 hours under perfectly dry conditions owing to the possession of accessory air-breathing organs. During very hot weather they get themselves buried in the mud.

If prevented from coming to the surface by exposing a perforated diaphragm across the water of the aquarium these fishes become very much agitated, beat against the sides of the aquarium and try their utmost to force out the diaphragm with their snout, their aquatic mode of respiration slackens and they show very violent convulsive symptoms till at the end of an hour or so they get "drowned" or asphyxiated.

Different species also behave differently during the drowning-period, and this varies considerably with the kind of water used.

After partial drowning the fish can be again revived by artificial



respiration. Injury to any particular portion of the accessory air-breathing organ has a marked effect on the "drowning" of a fish.

40. On the blood-vascular system of a common indian carp, Rohu (*Labeo rohita*).

P. SEN and B. K. DAS, Calcutta.

So far the anatomy of this common North-Indian teleost has not been worked out. The authors intend to give a complete account of the mode of arrangement of the various systems of this fish with a view to suit the college curriculum, but have at present confined their attention to the vascularity in general. In this connection there are several interesting features as regards the structure of the heart, the disposition of the afferent and the efferent branchial vessels, the formation of the renal-portal and the hepatic-portal veins, the curious origin of the posterior cardinals, the anal fin-loop and the single jugular vein.

Blood-vessels to the gonads as well as to the gas-bladder are worthy of note.

The interesting modification of caudal circulation as distinguished from other carps, and the formation of the hypobranchial arteries deserve special mention.

41. On the growth of scales in the rainbow trout (*Salmo irideus*).

D. BHATIA, Ludhiana.

The number of circuli or concentric ridges on scales obtained from a particular area of a growing rainbow trout depends on the size (weight) of the fish irrespective of its age or length.

Specimens under experiment were fed throughout a summer, a winter and next spring. They do not show any formation of the so-called "periodic-rings" on their scales. All the circuli formed correspond to the summer type, and the so-called "winter rings" were not at all formed during winter. It proves therefore that food is the principal factor which controls the formation of the rings on scales.

The rings though not uniform in width show no correspondence to the seasonal variations of temperature. Broad rings may be formed in summer, and narrow rings in winter (when the fish is fed throughout the year). The broad or narrow rings do not form any bands, for they occur quite irregularly on the scales. Their formation probably depends on the periods of maximal or minimal growth, which again depends mostly on the periods when the fish takes more or less food. Therefore, the chief factor concerned in the formation of the broad or narrow "summer and winter rings" is the abundance or scarcity of food, and not the rise or fall of temperature.

42. On the growth of the muscle cells in the developing fish—*Salmo fario*.

D. BHATIA, Ludhiana.

In the first stages of the larval development, the yolk-sac remains attached to the embryo, and the growth of the latter takes place at the expense of the yolk absorbed. The muscle-cells simply undergo an increase in size. This growth is relatively much more rapid than the growth of the whole embryo. No cell division seems to occur. The muscle cells already formed when the larva hatches simply increase in size. The growth of the embryo is therefore almost entirely dependent on the growth (enlargement) of the muscle cells.

But as soon as the larva begins feeding, and the yolk absorption



is diminished or finished, the development of the muscle tissue is brought about in two ways—cell growth and cell multiplication. With the beginning of the adult life of the brown-trout, there is an appreciable, though gradual fall in the relative cell growth of the muscle cell, although the fish itself is growing quite rapidly to an enormous size, so that the cell growth cannot keep pace, as it were, with the body growth. This difference in the relative growths of the two is made good by the increase in the number of cells, which occurs in an increasing degree as the development proceeds. So that the muscle cells grow in size as well as more cells are formed, either by division of the pre-existing ones, or the proliferation of new cells. And gradually, the phenomenon of cell growth yields to the phenomenon of the cell-multiplication to account for the growth of the fish body. The appearance of muscle cells dividing amitotically becomes more and more common in the latter part of the development.

43. Comparative morphology and anatomy of the Bombay marine slugs (Onchidiidae).

P. R. AWATI, and K. R. KARANDIKAR, Bombay.

A joint paper by the same authors on the systematic position of the Bombay marine slugs (Onchidiidae) was submitted to the last Indian Science Congress. The present paper is a continuation of the same.

This paper is split into two parts; the first part deals with morphology and anatomy and the second with embryology and bionomics of the three species belonging to two different genera, *Onchidium* and *Onchis*. Only the first part is submitted before the present Science Congress.

In this paper detailed anatomy and morphology of *Onchidium verruculatum* is described and is compared and contrasted with that of the other two species as far as the important features are concerned.

44. *Anthophora violacea* Lepel.

G. R. DUTT.

In his key to the different genera of the family Apidae (now treated as Super-family Apoidea), given on pp. 414-415 Fauna British India, Hymenoptera Vol. I, the late Col. Bingham placed the genus *Anthophora* under bees possessing three cubital cells in the forewing and a six-jointed maxillary palpus. In *Anthophora violacea* it has been ascertained that the maxillary palpus has only five joints. This peculiarity naturally causes some confusion to the beginners who, following Col. Bingham's arrangement, place *Anthophora violacea* under *Melecta*, the only genus mentioned by Bingham with a five jointed maxillary palpus. Some suitable changes to amend the Key have been suggested.







# INDIAN SCIENCE CONGRESS.

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Seventeenth Annual Meeting,  
ALLAHABAD, 1930.

ABSTRACTS OF PAPERS,  
Section of Agriculture.

*President :—George Clarke, Esq., C.I.E., F.I.S., F.C.S.,  
M.L.C.*

CALCUTTA.  
ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Agriculture.

### *Abstracts.*

#### SOIL IMPROVEMENT.

1. Further experiments on the preparation of organic manure.

GILBERT J. FOWLER, H. S. CHATURVEDI *and* R. N. JHRI.

During the past year the experiments have been continued with special reference to the following problems:—

- (1) In what way can cow's urine be most economically conserved and utilised?
- (2) Does the use of "activator" in any way facilitate the fixation of atmospheric Nitrogen?
- (3) Is it possible to acclimatise in India leguminous plants which have been found of value as green manures in other countries?
- (4) How can such plants best serve as raw material for composts?

It has been found that while cow's urine is an important agent for facilitating fermentation it appears to play no part in the fixation of Nitrogen.

On the other hand there is evidence that the presence of "activator" induces quick rotting and also fixation of Nitrogen.

Two out of three leguminous plants tried were successfully grown.

2. Studies on soil Actinomyces. Part IV.

P. K. DE, Bangalore.

The investigation was undertaken with the object of ascertaining the rôle played by Actinomyces in the decomposition of complex organic matter in the soil. This paper deals with the utilisation of different carbohydrate culture media by Actinomyces. Of the three strains that were studied, viz., A-Scabis, A-Chromogeus, A-Albosporeous, the last one was found to be most active, using up different carbohydrates in the following decreasing order—starch, glucose, canesugar, arabinose, cellulose. Influence of different concentrations of carbohydrate materials, reaction of media, and different nitrogen sources on the assimilation of carbohydrates by the organisms have been studied.

3. The decomposition of organic matter in water-logged soils.

N. DESIKACHAR, Bangalore.

Decomposition of different types of plant materials in soils was studied. Distribution of carbon and nitrogen in different forms and its relation to soil conditions were determined.

4. Periodicity of the nitrate content of soils.

L. S. NIGAM *and* H. N. BATHAM.

The paper deals with the data obtained in different countries of the world regarding the seasonal variations of the nitrate content of soils



along with those of the authors and the conclusions drawn are the following:—

1. That the greatest accumulation of nitrates takes place during summer months and the least during winter ones.
2. That there seems to exist a close relationship between the fluctuations of nitric nitrogen content of soils and different seasons of the year.
3. That the solar activity, which appears on the earth in the form of different seasons of the year, appears a most important factor in controlling the nitrifying bacterial activity in soils.

## 5. Nitrogen fixation in 'Kalar' soils as influenced by different Calcium treatments.

V. A. TAMHANE and P. G. KRISHNA, Sakrand (Sind).

It was intended to study the effect of the application of various forms of calcium salts on Nitrogen fixation in 'Kalar' soils at Sakrand in conjunction with the work on the effect of these salts on the plant growth. Also Nitrogen fixation in liquid media containing the various salts in the same proportion as found in the water soluble salts in the 'Kalar' soil, was studied. The following calcium salts were added to both the media to have ca. .2% equivalent:—Calcium Oxide, Chloride, Carbonate and Sulphate.

In solid media (soil) .2% calcium equivalent of Calcium Chloride and Calcium Sulphate treatments had stimulated nitrogen fixation; while Calcium Carbonate and Calcium oxide treatments had depressed the nitrogen fixation, the carbonate to a much less extent than the oxide. No relation was found between these effects and the reactions of the soils with the different treatments.

In liquid media .2% calcium equivalent of Calcium Carbonate and Calcium Sulphate had stimulated nitrogen fixation. The carbonate much more than the sulphate. Calcium chloride treatment had depressed the nitrogen fixation, while in the case of those treated with calcium oxide there was hardly any nitrogen fixation, and no bacterial growth was observed in these flasks. The initial reaction and its subsequent changes seem to be responsible for these observed effects.

Azotobacter strains were isolated from this soil and are being studied.

## 6. Correlation studies of the Punjab Soils.

MEHTA MUKAND LAL and R. P. SARATHY, Lahore.

The data on the Punjab soils by Lander, Ramji Narain and Mukand Lal has been studied statistically and certain significant correlations are found to exist between certain soil constituents.

Soil characteristics of different types of soils suited to different crops have also been brought out.

## 7. A biochemical study of soil treated continuously with sewage.

N. D. ACHAR and N. V. ACHAR, Bangalore.

Physical, chemical, physico-chemical and microbiological changes taking place in soil treated continuously with sewage have been studied.



8. Study of movement of water and soluble salts in the soils at the Agricultural Research Station, Sakrand (Sind). Part II. Study with repeated doses of irrigated water.

V. A. TAMHANE, J. A. DAJI and P. G. KRISHNA,  
Sakrand (Sind).

The first part of this paper dealing on single doses of irrigation water for leaching out soluble salts was read at the last Science Congress. In this paper are reported the results on the application of varying amounts of irrigation water with varying periods of interval between irrigations, to make the total amount of irrigated water to 29 inches. Also are included the data obtained from the same plots after a lapse of two years from the period of experimentation.

Repeated doses of irrigated water were effective in leaching out some of the soluble salts. As far as the soluble salts are concerned, a smaller dose of water given more frequently (for instance 2" every 10 days) was found to be more effective than larger doses given at longer intervals (for example 3" every 15 days). The irrigated water drained off well beyond a depth of five feet, indicating that leaching out of soluble salts in such soils would not be a very difficult matter. There was no deposition of the soluble salts in any of the soil strata to a depth of 6 feet. Translocation of the leached salts to the surface layer would not occur if these salts are leached into the lower soil strata (below a depth of 5 feet), unless the water table rises very close to the surface soil layer. In such soils wherein appreciable amounts of Calcium Salts are present, Sodium salts are leached to a greater degree than Calcium Salts, and of the Sodium Salts Sodium Chloride is most easily leached out from the surface soil layer.

9. Reports for reclaiming Usar lands of the United Provinces.

L. C. SHARMA.

The total area of Usar lands in the United Provinces of Agra and Oudh amounted to 3,129,053 acres in 1888. The principal salts which made these lands unfit for growing crops are sodium carbonate, sodium sulphate and sodium chloride. Such lands are generally heavy clay soils and very often termed as *parti* or waste lands. The experience gained in the past shows that the more vigorously they are cultivated, the more perfectly are the said salts prevented from accumulating at or near the surface and that they are capable of being reclaimed without incurring any heavy expenditure.

The Department of Agriculture, U.P., carried out a series of experiments for reclaiming Usar lands at various centres in the Provinces, some of which proved a marked success. Certain methods for reclaiming Usar lands under trial at the Experimental Station, Partabgarh, are found very encouraging and highly appreciated by a number of zamindars and cultivators who also tried them for reclaiming their Usar lands. These methods are mentioned in the article of which this is the abstract.

10. Hard calcareous sub-soils in South Bihar. Their morphology and treatment.

M. N. GHOSH, Sabour.

These sub-soils exist generally in South Bihar to very great depths at some distance from the Ganges channel. They form parts of the older Gangetic alluvium and their hardness is due to the formation of compact



gels by the absorption of lime carbonates by the soil colloids. Whenever they come near the surface the land becomes infertile. Continuous cultivation improves the land but the improvement is not much apparent within two or three years, but very visible improvement is noticed by treatment with sodium salts preferably nitrate of soda which seems to attack the gels and break their compactness.

## 11. Note on electric farming.

S. S. NEHRU, Rae Bareli.

Tests have been made under—I. Seed Energetics;  
II. Soil Energetics;  
III. Both.

*Under I*, various seeds were energised by high-tension electric sparks (1000 to 10,000 volts) for 5 to 10 minutes and sown in test plots, control plots being sown with ordinary seed.

*Under II*, different soils from loam to sand were energised by means of a "tickler" or discharge-tube through which air was pumped and sparked at the orifice. Its conical nozzle was driven into the soil at various points and sparked air pumped for 2 to 5 minutes every time.

*Under III*, the methods of I and II were combined.

Tests have been made with *Sanai*; *Mustard*; *Wheat*; *Cauliflower*; *Salad*; *Mango Seedlings*; *Juar*; *Broomcorn*; *Bajra*; *Zinnia*; *Chrysanthemum*; and *Gomphrema*.

Every seed, plant and soil has responded to treatment, most actively the cereals, then mustard and sanai. Flowers have also reacted notably. For example: Energised Juar grew from 81 to 280 Cm. control from 101 to 215; Energised Broomcorn from 115 to 340, control from 115 to 264. Energised Bajra has developed more ears than the control one. Flower-plants have yielded more numerous and bigger flowers. Unseasonal sowings, energised, have thriven; while control ones died out.

Tests continue.

## 12. Kudzu Vine (*Pueraria thunbergiana*).

N. V. JOSHI, Pusa.

Kudzu vine was grown and kept under observation for three years and the results of the experiments are given below :—

1. Kudzu Vine is a very promising perennial crop.
2. It has been grown from imported seed but it can be better propagated from runners which develop rootlets at the nodes during the rains. Kudzu is slow to cover the ground but when once established it thrives under drought as well as excessive rain.
3. The germinating power of the seeds rapidly deteriorates. April is the best time for growing it from seeds and August and September for propagating by rooted runners.
4. Its growth in the early spring growth makes it particularly suitable for growing for pasture or cutting it for fodder.
5. It is a heavy yielder and grows quite well on land near the hedges or trees.
6. Kudzu is well worth the trial for grazing on poor rocky soil as well as in places where only Kush and other grasses grow and in places liable to be under water like the Dhab areas.
7. If grown on cultivated soil Kudzu is difficult to eradicate entirely from arable land the first year such land is needed for other crops.
8. It contains, as an average 0.4 to 0.5 per cent. nitrogen and in case any cutting is not required for feeding stock it may be utilised for green manuring.



9. The use of its stem for fibre is well worth investigating.
10. Its roots contain about 40 per cent. starch.
13. A preliminary note on the surface run-off and soil-erosion.

N. V. KANITKAR and G. M. BAPAT, Poona.

The authors have conducted experiments to determine the surface run-off of rain water and soil erosion during the monsoon season of this year at Manjri Dry Farm Experimental Station. The difference in run off and erosion under three different treatments of soil are studied with one definite gradient of three in hundred. The area of each plot is half a guntha or  $1/80$  of an acre, and each plot is separated from the other by a partition of galvanised plane iron sheet fixed 9" deep in the soil on three sides. Masonry tank is built at the lower end of each plot in which water and silt are collected after each day's rain. The results are summarised below :—

- (1) The total rain-fall from June 1st to 10th October 1929 amount to 17.06 inches received in 63 rainy days.
- (2) Only on eleven days the rains caused run-off of water and soil erosion.
- (3) The largest run-off took place from the ploughed plot, the harrowed and untreated being next in order. The difference was more marked at the beginning but later on all plots behaved very similarly.
- (4) The quantities of silt removed were again highest in the ploughed plot, untreated and harrowed coming in order.
- (5) The quantities of water lost by run-off varied from 34 to 38 per cent. of the total rain-fall of the season and nearly 50 per cent. of the useful rain.

14. The effect on the soil complex of applications of sodium nitrate to swamp paddy soils.

B. VISWA NATH and S. KASINATHAN.

Continued applications of sodium nitrate does not alter the cationic composition of the clay-complex and the beneficial effects of the manure are due in large measure to its powers of flocculating the soil colloids.

15. Determination of exchangeable calcium in calcareous soils.

S. KASINATHAN and B. VISWA NATH.

The need for a reliable method of determining exchangeable lime for soils rich in carbonate is emphasised. Based on the influence of bicarbonate concentrations on the solubility of calcium carbonate, one such method has been evolved.

## THE ORGANIZATION OF AGRICULTURAL RESEARCH.

16. The Organization of Agriculture Research.

ALBERT HOWARD and GABRIELLE L. C. HOWARD, Indore.

One of the problems of the moment, in the organization of agricultural research in the Empire, concerns the possible division of the work between the local and the central institute. Most attempts in this direction have failed in the past and are likely to fail in the future for the reason that the problem is not based on the merits of the case but



has arisen either through accidents of administration or from failure to realize what successful research work in agriculture entails in the way of staff and facilities. The solution of the problem becomes much easier if the artificial sub-division of the subject, into long-range and local problems, is given up and the more natural one of research and demonstration is adopted in its place. The ideal system of conducting agricultural research in India and other parts of the Empire appears to lie in the simplification rather than in the elaboration of the organization. Any attempts to overstrain system of organization in the hope that they may replace competent investigators can only end in failure. In research the man is everything ; the organization is a minor matter.

### 17. The Indian Universities and the improvement of Indian Agriculture.

B. C. BURT, Delhi.

As the result of developments on both sides the position is now more favourable for co-operation between the universities and agricultural research institutes than in the past since most agricultural colleges are affiliated to universities and many universities have raised their standard of teaching in pure science and made definite provision for scientific research. There is ample room for co-operation between the universities and those engaged on the improvement of agricultural practice and the Imperial Council of Agricultural Research, on which the universities are directly represented, affords a new opening for such co-operation.

### 18. The Imperial Council of Agricultural Research, its constitution, aims, and functions.

SIR T. VIJAYRAGHAVACHARYA.

The Imperial Council of Agricultural Research has been set up as a result of the recommendations of the Royal Commission on Agriculture in India. Its functions and constitution and aims are described and particular attention is drawn to the fact that it is an all-India body on the Governing Body of which each province is represented by its Minister of Agriculture, the Central Legislature by three elected representatives, and commercial interests by one representative each of the Associated Chambers of Commerce of India and Ceylon and the Federation of Indian Chambers of Commerce. There is also legal provision enabling Indian States to be represented. The Advisory Board is a technical body containing representatives of the agricultural and veterinary departments, universities, research institutes and other bodies engaged on scientific research. The research Council has been registered as a society and has funds of its own for the promotion of research, the dissemination of scientific, technical and economic information and for the assistance of post-graduate training in agricultural science. At present the greater part of its funds are provided by the Government of India but a munificent donation of 2 lakhs has been made by the Hyderabad State and other benefactions are hoped for. The Research Council has no research institute of its own and will promote research by grants to existing institutions for specified investigations.

### THE INDIAN SUGAR INDUSTRY.

#### 19. Problems of the indigenous sugar industry of India.

KHAN BAHADUR SYED MOHD. HADI, Bhopal.

The paper deals briefly with the past and present condition of the indigenous Sugar Industry and the trade in Indian sugars. It points out



the reasons which led to the gradual decline in the industry since the import in considerable quantities of foreign sugars began. An account is given of the researches made in Bhopal with a view to obtaining a much larger recovery of sugar from S. 48 and a number of Coimbatore seedlings and exotic canes than is possible under the Rohilkhand system. Improved methods of growing superior varieties as "plant" and ratoon are described. It has been shown how by the use of efficient mills for crushing the cane, of a standard and an auxiliary plant of special design for boiling the juice and of a high speed centrifugal of special construction for curing the massecuite, from 7 to over 8 per cent. on cane, of white sugar of good quality (1st and 2nd) can be produced with no expensive appliances or high technical skill, in villages, at a cost which would enable the Indian manufacturer to hold his own in the competition with which he is confronted.

## 20. Results and object lessons from a half century of cane breeding.

NOEL DEER.

An account of the development of sugarcane breeding is given since the rediscovery of the fertility of cane seed by Soltwedel and by Harrison and Bovell.

Special reference is made to the work in Java culminating in the production of P.O.J. 2878 and to the work initiated by Barber in India.

The value of, and the necessity for, the continuance of this work for Indian Agriculture is pointed out.

## 21. Suggested method of studying sugarcanes for breeding work.

KIDAR LALL KHANNA and RAO BAHADUR T. S.  
VENKATRAMAN, Coimbatore.

The life histories of three cane varieties up to the end of about 20 weeks from time of planting are given in some detail.

The three varieties are *Katha*, indigenous cane of the Punjab, Co. 205, replacing *Katha* chiefly in the unirrigated tracts of the Punjab and Co. 285, a future rival of Co. 205 and a distinct improvement over *Katha* and Co. 205.

The studies include the number, development and functioning period of 'sett' roots, the periodic developments of 'shoot' roots, bud germination and the bending of the main and subsidiary shoots at different stages of growth.

A correlation is indicated between shoot root development and tillering.

The growth periods of the varieties are examined and it is found that the shoot growth is correlated with root development.

The first fourteen to twenty weeks represent a rather critical period for sugarcanes in the Punjab; and, on account of their thriftier shoot development, the Coimbatore seedlings are better adapted to this period of unfavourable conditions than the indigenous canes.

It is suggested that studies of developmental stages and characteristic of growth would be of considerable use in the selection of canes for particular localities; and such studies are an important aid in sugarcane breeding.



## 22. Sugar industry in India as compared to those of other countries.

K. C. BANERJI, Allahabad.

The object of this communication is to study the conditions which govern the Sugar Cane Industry of different countries, such as Java, Hawaii, Philippines, etc., in order to find out a basis of comparison whereby to fix a place for India in the international competition. Indian industry according to modern methods has only been considered. The system of cane supply, control in cultivation and factory work, Central Organisation, etc., in different countries have been discussed and an attempt has been made to find out a solution for improving the present condition of the Indian Cane Sugar Industry. The control figures of the milling and boiling houses in different countries have been discussed with reference to special machinery employed in those countries.

## 23. Tilling, planting, and manuring of sugar cane fields in Java.

K. C. BANERJI, Allahabad.

The high land lease and the impossibility of growing ratoons necessitate the cane sugar industry of Java to get the highest possible output from unit planted area diminishing the cost of production. The cultivation has to be made as intensive as possible. Reference has been made to the highest degree of the tilling of the soil, specially to the Reynose system, and also ploughing system, labour being cheap and abundant in Java. The tertiary sugar cane soils belonging to the miocene layers in their three formations have been discussed. The paper will give a short survey on planting, its usual method and the materials used. (Bibit, Bergbibit, Rajoengan, etc.) There is also a brief account of the essential change in the planting material caused by the introduction of POJ 2878 on a large scale. Lastly general remarks on manuring have been made with discussions on the following classes of manures as used in Java, on their advantages and disadvantages;—Nitrogen containing manures, Phosphate containing manures, combined manures, Inorganic manures, organic manures, Green manures, etc. The time, form, manner, and amount of the manures to be administered have also been discussed.

## CROP PRODUCTION.

## 24. The classification of the cultivated rices in the United Provinces.

R. L. SETHI, Cawnpore.

While handling a fairly large number of rice varieties in the United Provinces, and noticing that the subject had not been studied before from a systematic point of view in these provinces, the necessity of a scheme of classification became apparent. 1200 samples were collected from different districts of the province, and a thorough pure line selection was continued for five successive years, when ultimately 135 types were selected as pure varieties possessing constant characters. On making a complete study of various characters of the rice plant it was found that the characters of the grain are more constant and more useful than other vegetative and agricultural characters. These grain characters (colour, size and shape) have consequently been employed as the main-heads of the present scheme of classification. A history of the previous work on classification has been given, and reasons for employing grain characters as a basis of classification are enumerated. The volume of the grain has



also been measured, and the relationship between the size of the grain and that of the volume is shown. The product of the length  $\times$  breadth of the hulled grain harmonizes with the volume, and the former divided by the latter equals 1. The scheme of classification and the grouping of varieties is shown, and various distinctive shapes of the rice grain found in the United Provinces are described.

## 25. Disturbing factors in flowering and fruiting capacity of the cotton plant in United Provinces.

B. RAM PRASAD.

Total number of bolls per plant is the result of the number of flowers setting throughout the flowering season. In order to correctly arrive at the differences in the flowering capacities of 2 particular varieties, a count of the actual number of flowers each day was made throughout the season on the ten best flowering plants for three years.

In spite of the variations found in the number of flowers per day on account of varietal differences, the number appearing each day is also influenced by the bright or the cloudy conditions of weather prevailing in the flowering season.

Each boll contains about 2 grams of cotton. In order to obtain a good average yield of say 8 maunds per acre we should have only about 7 bolls per plant on an average with a spacing of 2 from plant to plant and same distance from line to line if all other conditions remain ideally favourable.

The 30 days' period from 2nd week of August till 2nd week of September is the most favourable period for setting in early cottons. If there is a disturbance during the period the crop suffers but favourable conditions tend to give better outturn per acre.

## 26. Classification of Indian cottons.

G. L. KOTTUR.

The indigenous types of cotton cultivated in this country are classified into 3 species on the basis of colour in the leaf as *Gossypium herbaceum*, *Gossypium neglectum*, and *Gossypium sanguinum*. The leaf in *G. herbaceum* is yellowish green without any basal spot, in *G. neglectum* dark green with red spot at the base, and in *G. sanguinum* reddish green, both the basal spot and the veins being red. Each species is further divided into a number of sub-divisions on the characters of lobing, colour of flower, stem, habit of growth, hairiness, bracts, size of flower, boll, seed ginning percentage and staple length. These divisions enable us to clearly distinguish all the cottons now cultivated in the country. The possibilities of new types coming into cultivation as a result of hybridisation are considered and the present classification is deemed to be sufficiently wide to include them.

## 27. Improvement of Sind *deshi* cotton.

K. I. THADANI and B. B. MULCHANDANI, Sakrand (Sind).

1. Sind *deshi* cotton consists of a mixture of four *neglectum* varieties differing in the colour of the flower which may be yellow or white, and the nature of leaf lobes which may be narrow or broad in addition to several other characters. The yellow flowered types preponderate to the extent of 70 per cent.

2. When two pure strains differing in the colour of flower were grown in alternate rows, the incidence of natural crossing showed that (i) about 16 per cent. of the plants got vitiated, (ii) about 6 per cent. of the



flowers got crossed, (iii) about 3.3 per cent. of the ovules showed cross pollination, (iv) natural crossing took place from 3 to 22 feet. White flowered plants picked from a field where yellow flowered types preponderate as mentioned above showed that 50-84 per cent of them had got contaminated.

3. Unit selection in Sind *deshi* cotton has resulted in the production of a strain of roseum cotton known as 27 W.N. which is capable of (a) yielding over 20% more kappas per acre than ordinary seed, (b) early crop, (c) 5 per cent. higher ginning outturn, (d) greater premium over ordinary cotton on account of rough feel and bright colour of cotton. This cotton is now the standard *deshi* cotton of Sind. The seed multiplication scheme consists of (i) selfing patch sown with selfed seed of single plants, (ii) seed patch of an acre and a half, (iii) seed farm area of 30 acres, (iv) developmental zamindari area of 300 acres, (v) registered growers area of 3000 acres, (vi) Taluka developmental area of about 60,000 acres. Each stage is fed by the preceding stage and thus purity is maintained. The scheme is progressing and expanding every year.

## 28. Cultivation of Broomcorn in India.

S. S. NEHRU, Rae Bareli.

In the *last paper* at Madras, results of successful tests with Indian broomcorn under European, African and American conditions were communicated. Encouraged by the good results obtained, the same selectivised, hardened and resistant seed has since been supplied to 7 Government Farms, 11 Taluqdars' farm and 6 other private farms in India. The Government Farms are in Muttra, Partabgarh, Rae Bareli, Poona, Gwalior, Dharwar and Sholapore. The Taluqdars' farms are mostly in Rae Bareli district. The private farms are in Allahabad, Cawnpore, Jhansi, and Lahore. Thus, tests with broomcorn are being made in all representative parts of the country.

Results to date show cent per cent. germination everywhere in 3 to 6 days and in all soils ranging from sand to clay. Broomcorn has grown under all conditions, even when local *sorghums* have failed. And the growth has been notably rapid, the plants in a characteristic field measuring 1'-8," 3'-8," 5'-10," 7'-10," 8'-5," 10'-5," and 12' in the first seven fortnights respectively. A very healthy plant with tall stalk, thick base and long panicles has been obtained.

Further results will be communicated subsequently.

## 29. The growth of the cotton plant in India--II. The predetermination of subsequent growth variability and variation in the "growth resistance potential" at the early seedling phase, and its explanation in terms of external factors (temperature) and internal conditions (hydration of growing tissues).

R. S. INAMDAR and B. N. SINGH, Benares.

1. *The outlook and the procedure*:—This series of investigations was instituted with a view to study the growth mechanism of plants, choosing an economic plant for the purpose, viz., cotton. For obtaining the requisite variability of growth reactions for an estimation of internal factors, the atmospheric factors of the environment were used as the variables. The variability of the atmospheric factors was secured by growing the plants under *field conditions* in series at successive intervals of a fortnight in the summer of 1925. The factors of the substratum, such as, the moisture content and the "nutritional" constituents, were kept above the maximum demands which the plant is believed to be



making on the substratum. A full record of atmospheric factors was obtained from the local Meteorological Station.

The results now described throw additional interesting light on the growth mechanism of plants for theory and practice, and also emphasise the significance of *hydration factor in growth and senescence*.

Organismal growth variability was also designed by growing two different varieties of cotton, viz., *Dhulia neglectum* and *Gossypium herbaceum*. The results are described below separately.

Growth magnitudes were measured in terms of the dry weights produced by the entire plants and its organs (including the reproductive organs). The extent of the assimilating and the transpiring surface and the march of the respiratory intensity as growth proceeded, were also recorded at corresponding periods of growth. Though the results are not described here, they have, nevertheless, been utilised in arriving at the final conclusions.

From a quantitative analysis of growth data, an analysis is attempted of the growth mechanism and the approach of senility, including the nature of reproductive growth as opposed to vegetative growth.

Interesting and striking conclusions emerge from these studies on the economic side of the growth of the cotton plant and of crop plants in general.

2. *Summary of results and conclusions* :—The time growth curves are of the usual sigmoid type and conform, on analysis, to a variation of the exponential type of the equation of the form,  $\text{Log } W = n \log t + a$ , where  $W$  = dry weight,  $t$  = days after germination, and  $a$  and  $n$  = constants. Therefore a straight line is obtained when  $\text{Log } W$  is plotted against  $\log t$ . The slope of this straight line is made a measure of the march of growth towards senescence in each series of sowings.

Curiously the gradient of the march of growth remains identical in all the series, inspite of variations in the atmospheric environment. Consequently the *relative rates of growth* are identical in all the series in corresponding periods of growth.

But growth variability is manifest in different series in many directions (see below). *This variability is, therefore, predetermined at a very early seedling phase of growth* (which is the critical stage in growth) in response to external conditions.

The predetermination leads to a series of resistences to growth in the subsequent march of growth toward senility, in accordance with the environmental conditions to which the plant becomes subject. Therefore the term "*Development of Growth Resistance Potential*" is given to this early predetermination.

The degree of predetermined resistance to growth at the early seedling phase carries the downward march of the relative growth rate curve to zero intensity sooner or later in different series of sowings and determines the period of approach of senility and the final stoppage of growth as also the number of times the flower buds appear in the course of growth in each series.

Growth variations in different series of sowings are manifest under five headings, viz., (1) variations in the final dry weights in corresponding periods of growth, (2) The occasional sudden breaks in the growth of plants, especially when the first reproductive initials are laid down, (3) the relative retardation of the development of reproductive primordia (including the shedding of flowers and bolls, (4) the number of times the reproductive primordia appear, and (5) the period of approach of senility and the final stoppage of growth.

All these growth variations reduce themselves to the resultant effects of one primary variation, viz. differences in the resistences to early growth (production of dry matter) within about 30 days after germination. The subsequent variations are the resultant effects in various directions of the superimposition of the later atmospheric conditions on this primary variation.



Therefore the early predetermination consists in the change in the seedling phase which leads to the primary variation, the development of varying degrees of resistance to the early production of dry weight. The predetermined change is a *potential* for the subsequent development of growth resistance.

The "growth resistance potential" is explained in terms of two significant variations, (1) variation in the "growth potential" of the growing cells in the early meristem, and (2) variation in the number of cells available for cell division and growth.

Among causative factors in predetermination, temperature effects appear to be the most important. Radiation effects do not assume significant proportions in the open in the tropics.

It is suggested that one of the effects of temperature is to introduce variations in the number of cells available for cell division and growth in the early meristem.

Of the many internal conditions, the hydration factor of the growing meristem appears to play a very important part in contributing towards the final change. It is suggested that variations in this factor are introduced in the early predetermining phase of growth by variations in the intensity of transpiratory loss of water.

This hydration factor appears to play also a very important part in the approach of senility and the final stoppage of growth. It is suggested from independent investigations on the specific conductivity of plants with monopodial and sympodial modes of growth that the hydration of growing tissues is influenced by as growth proceeds.

*The control of the germination stage is of paramount importance.* This done, "Out of season" growth also may prove successful within certain limits.

So far as the locality of Benares is concerned, the high yields obtained per plant justify the earlier conclusion that cotton can be grown very successfully in this tract. The requisites are that very early sowing in the beginning of summer should be accomplished and the plants maintained by irrigation till the monsoon rains commence. The short-growing variety gives bumper yields under these conditions.

30. The growth of the cotton plant in India—III. The relation of reproductive growth to vegetative growth as judged by the growth curves in *Dhulia Neglectum*. The physiological significance of maximal humps in growth rate curves antecedent to successive initiations of reproductive growth.

R. S. INAMDAR and B. N. SINGH, Benares.

This paper deals with the relation of vegetative growth to reproductive growth and the explanation of variability of reproductive growth in terms of internal conditions and previous growth history.

Part I of this series established a close connection between the appearance of a maximal hump in the relative growth rate curve and the appearance of reproductive buds. This is confirmed in the present series which indicate 2 or 3 maximal humps in the generally descending growth rate curves in each series, each time antecedent to the appearance of reproductive buds.

Evidence is accumulated by the second author elsewhere that the period of each maximum in the relative growth rate curve is also associated with a corresponding maximum in the respiratory index of the growing meristem, and in the general constructive activity of the protoplasm (relating to both carbon and nitrogen anabolism).

*These maxima have a deeper physiological significance in that those periods are characterised by a general increase in the metabolic activity of the*



*protoplasmic complex*. It is also concluded that the periods of appearance of maximal humps are also the periods when the reproductive initials are laid down internally, though their emergence as visibly recognisable structures externally is more or less delayed depending upon the "nutritional" balance available in the plant.

Part I of this series of communications indicated that the period of first emergence of reproductive buds is liable to vary in different sowings. The present series of sowings being made in only one season, viz., the summer, this variation is negligible (the period of first appearance of flower buds ranging from 47 to 52 days after germination in all the series).

The period of emergence of reproductive buds as visible structures is made up of two component phases, viz., (a) the *initiation* of reproductive phase (as judged by the maximal humps on the growth rate curve), and (b) the *development* of reproductive primordia into externally visible flower buds.

(a) The *initiation* of the first reproductive phase varies in all the four series of sowings (38, 27, 25 and 24 days after germination respectively). This variation is correlated with an *inverse* variation in the antecedent production of total dry matter in each series. The period of *initiation* of reproductive phase in each series is, therefore, correlated in some way with predetermination in the seedling phase.

(b) The interval between the *initiation* of reproductive phase and the *emergence* of reproductive buds as externally visible structures (9, 18, 25 and 26 days respectively in all the four series) varies, however, in the *same* direction as the antecedent production of total dry matter in the plants. This phase is, therefore, directly correlated with the "nutritional" balance between the vegetative and the reproductive growth.

This contrast in the behaviour of the two phases also confirms the conclusion that the primary cause for the *initiation* of the reproductive phase is much more deep seated than mere balance in nutritional flow.

The periods for the subsequent successive incidences of reproductive growth after the appearance of the first reproductive phase remain constant for each interval in all the series, in spite of varying development and complete or partial shedding of flower buds and bolls. It is, therefore, concluded that the *initiation* of the reproductive phase introduces a *physiological inhibition* of growth activity, which is not wholly connected with the diversion of nutritional flow to the developing reproductive structures and which takes a definite amount of time to be washed off.

The number of times the reproductive growth occurs depends upon the total span of life determined by the downward gradient of the relative growth rate curve reaching the zero-line.

The final yields obtained per plant are the resultant effects of these growth variabilities in each phase of vegetative and reproductive growth.

### 31. The growth of the cotton plant in India—IV. The interpretation of varietal variability of growth in *Gossypium herbaceum* as compared with that of *Dhulia neglectum*.

R. S. INAMDAR and B. N. SINGH, Benares.

A study of varietal variability was undertaken with a view to estimate growth factors.



It is concluded at the outset that under the conditions in Benares in the season in which it was grown, *Gosseypium herbaceum* with a longer period of growth does not attain to the maximum possibilities of its growth potentiality.

The growth curves in all the series conform, in their general features, to those of *Dhulia neglectum* when allowances are made for the disturbances introduced. Thus all conform to the equation  $\text{Log } W = n \log t + a$ . The disturbances introduced by the appearance of reproductive phases are of the same nature, emphasising here also the physiological significance of the antecedent maximal hump in the growth rate curve on the subsequent initiation of the reproductive phase. The effect of the atmospheric conditions on the successive sowings of the crop are also of the same nature.

The plant does not grow successfully because the maximum growth potentiality of the plant never comes into full play. Consequently the slope of the growth curve is always less steep than that of the corresponding curves in *Dhulia neglectum*. This affects primarily the physiologically comparable magnitudes of dry weights produced by the plants at physiologically corresponding periods of growth as compared with the growth of the shorter variety. This is also the reason why a large number of reproductive initials fail to develop to maturity (with an increase in the number of flowers and bolls that shed) because the requisite physiological balance between the vegetative growth and the reproductive growth is not kept up.

It is suggested that the failure of the plant to bring its full growth potentiality into play is to be located in the relative efficiency of the transpiratory and assimilatory functions of the leaf in this variety.

Resistance to growth increases, on the one hand, as the sowing time advances towards the height of summer with its rising temperature, and, on the other hand, as the early growth of plants is overtaken by the continuous monsoon rains. The former influences the "predetermining" phase of growth and the latter the assimilatory intensity of the leaves for early dry weight production. The constructional difference in the leaves of this variety as compared with those of *Dhulia neglectum* appear to be responsible for both these differences; and an independent enquiry in this direction may prove profitable.

32. The growth of the cotton plant in India—V. The causal factors at work in the shedding of flowers and bolls (which determine final yield in cotton) in terms of the conceptions of dynamic equilibria in the co-ordinated growth activity of the entire organism in successive phases of growth.

B. N. SINGH, Benares.

The preceding papers in this series of communications have established the view that growth magnitudes—whether vegetative or reproductive—have to be analysed in terms of the conceptions of dynamic equilibria in the co-ordinated growth activities of the plant in successive phases of growth. The influence of some of these growth activities is more deep-seated than others of the subsequent phases of growth. Nevertheless, the final results at any stage of growth are the resultant effects of a kind of integration of the previous happenings in the plant which lives in the present. In the present investigation this conception has been applied to the analysis of the important problem of flower and boll shedding in the cotton plant and of the final yields obtained.

Leaving apart parasitic pathology as an explanation of the shedding of flowers and bolls in certain instances, regarding the physiological



aspects of the problem, recent work has rather tended towards concentration on isolated phenomena as causal factors, ranging from the shortage of water supply or nutritive material to the developing flowers and fruits, to the incomplete pollination or fertilisation of the flower, or even the osmotic changes in the critical condition of the flower. But no serious attempt has been made to apply the principles of dynamic conceptions of growth activity of the organism as a whole to the analysis of the problem.

The first striking result in this way of analysis is the close connection observed between the percentage of flowers which reach maturity in each variety and each series of sowings of cotton, and the degree to which the *full* growth potentiality of the plant comes into play as the visible manifestation of growth. Thus, for instance, *Gossypium herbaceum*, has to its credit cent per cent shedding of flowers and bolls in the II<sup>nd</sup>, III<sup>rd</sup> and IV<sup>th</sup> series of sowings, while in *Dhulia neglectum*, the shedding is only 60, 70 and 40 per cents of production in the corresponding series of sowings.

The results of the four series of sowings of *Dhulia neglectum* are a further illustration of the dependence of the number of flowers which reach maturity on the previous growth history of the plants. Thus, for instance, the shedding of bolls is 30, 60, 70 and 40 per cents of production respectively in all the four series. These composite figures for the total growth period are remarkably correlated with growth variations in all the series in successive phases of growth described earlier (part II).

Some of these variations are deep-seated and are predetermined at the early seedling phase, while others are merely the temporary and superficial effects of the environment on the operation of predetermined factors in the plant in various directions, (Cf. series II and III). But in either case the end result in yield is the resultant effect of the dynamic relations of growth activities in different phases of growth.

The most convincing record of the existence of dynamic relations is obtained in the relations existing between the intensity of the maximal humps of the relative rate of growth antecedent to flower production in each series, and the total yield obtained from the subsequent crop of flowers. Figures are exhibited in this connection for each of the three phases of reproductive growth in both the short and the long variety series I.

Of the immediate antecedents to the shedding of flowers and bolls, the failure of the flowers to open has been noted prominently in the long variety, *Gossypium herbaceum*, series II, III and IV, where cent per cent shedding of flowers and bolls occurs. The failure of the flowers to open may affect either the maturity of pollen or the cross fertilisation of flowers, factors which are known to cause flower and boll shedding.

Of the other immediate antecedent factors, the water-content of the tissues appears to be significant.

The dependence of the maturity of flowers and buds on the supply of nutritive material in the vegetative parts is evident from the many facts which are discussed above. The data connecting the total dry weights produced and the final yields of cotton per plant in all the four series of *Dhulia neglectum* are a gross illustration of what has been analytically discussed above in every phase of growth. Thus, for instance, the relations of final  $\frac{\text{dry weights}}{\text{yields}}$  per plant are  $\frac{44.18 \text{ gms.}}{3\frac{1}{2} \text{ tolas}}$ ,  $\frac{29.88 \text{ gms.}}{2\frac{1}{2} \text{ tolas}}$ ,  $\frac{24.33 \text{ gms.}}{2\frac{1}{2} \text{ tolas}}$ , and  $\frac{39.11 \text{ gms.}}{3\frac{1}{2} \text{ tolas}}$ , respectively for the four series of sowings.

(average) (average) (average) (average)

These immediate antecedents, which are all true, have loomed large in recent investigations, while the problem is really deeper than all of them put together. The problem of the shedding of flowers and bolls is the



problem of analysis of growth variability in each phase of growth, which has been attempted in the study of the growth mechanism of the plant in parts I to IV of this series. If it is a phenomenon of physiological pathology of the plant, it is only in this sense; and its solution is the solution of how to bring the maximum possible growth potentiality of the plant into full play in each phase of growth.

### 33. A note on albino and mosaic characters in rice.

S. K. MITRA and S. N. GUPTA.

The albino seedlings are found to appear in a number of apparently pure varieties both in autumn (short growing) and winter (long growing) paddy varieties. Their percentage ranges from 26% in Asra (winter paddy) to 20% in aus crosses.

An apparently pure sali type, S. 559, with green leaves has been found to produce green, mosaic (white-striped leaves) and albino plants in a 12 : 3 : 1 ratio, as it were. The mosaic plants originating from the above also give out mainly mosaic, albino and a very few green seedlings. Both the albino and mosaic characters are degenerative and lethal. Attempts are being made to study the inheritance of same by hybridization.

### 34. Chlorophyll deficiencies in Sorghum.

G. N. RANGASWAMY AYYANGAR and M. A. SANKARA AYYAR.

Five types of Chlorophyll deficiency in Sorghum are described and recorded as simple recessives to the normal healthy green.

### 35. A comparison of the progeny of (1) shrivelled wheat grains, and (2) normal plump wheat grains.

L. JAI CHAND LUTHRA, Lyallpur.

In 1928 wheat crop in several parts of the Punjab was greatly damaged by adverse conditions and the wheat grain did not develop well and was shrivelled. In some cases the heads were found abortive and grain was not formed to the extent of 15-30 %. Germination capacity of the grain, though shrivelled, was found on testing to be pretty high. In over 50 samples it varied between 90-99 % and in most of the cases it was between 60 and 90 %. Samples from some bad fields, however, showed 20-50 % germination. As a result of these tests wheat grains though apparently imperfect and extremely small in size, were considered suitable for sowing purposes.

2. In 1929 experiments were laid down to compare the crop raised from shrivelled grains and normal plump grains. Five representative samples from different places were taken and the following results were obtained:—

The progeny of shrivelled grains showed a remarkable improvement over parent grains. Mean weight of 1000 grains had increased by 139.4 %. Specific gravity rose by 7.2 %; length was increased by 22.1 and breadth by 63.8 %. Consistency of the grain also had improved considerably. There was no sign of shrivelling and the grains were as plump as in normal condition.



## AGRICULTURAL ENTOMOLOGY.

## 36. The Aleyrodidæ on Citrus and their control in the Punjab.

MOHAMMAD AFZAL HUSAIN and ABDUL WAHID, Punjab.

The following species of the Aleyrodidæ have so far been found on citrus trees in the Punjab :—

*Dialeurodes citri* Ashm.

*Aleurocanthus woglumi* Ashb.

*Aleurocanthus spiniferus* Q.

*Aleurolobus marlatti* Q.

*Dialeurodes (Dialeurolonga) elongata* Dozier.

*Tetraleurodoides citriculus* Dozier (mn.s.n.).

*Aleuromigda dojhai* Dozier and Baker (mn.s.n.).

Of these the three last named species are new to science and have been named from the collection sent from the Punjab.

*Aleurocanthus citriperdus* Q. and B. collected by Woglum from Lahore has not been so far obtained by us.

External anatomy, life-history, seasonal-history and distribution have been studied.

*D. citri* and *D. elongata* are the commonest and the most destructive in the Punjab. *A. spiniferus* causes serious damage to citrus trees in Lahore. *A. woglumi* is destructive in South-East Punjab.

Except *A. marlatti* and *T. citriculus* which are found on the upper as well as the lower surface of leaves, all the species confine themselves to the lower surface of leaves. The eggs are laid practically invariably on the lower surface of leaves and the nymphs settle there. The 'honey dew' which these insects produce falls on the leaves below, and on this the black mould appears. The infested trees thus look black.

Damage is caused by the nymphs sucking the juice, but more particularly through interference in photosynthesis caused by the covering of black mould on the leaves. There is however no external mark of injury such as spotting, discoloration, curling, or drying. The pest does not bring about the death of leaves or shoots. A severely infested tree does not bear fruit and if it does bear any the fruit is insipid.

The pests have been controlled by spraying.

## 37. The cotton white-flies (Aleyrodidæ) and the cotton failures in the Punjab.

MOHAMMAD AFZAL HUSAIN, Punjab.

Since 1919 there have been five more or less serious failures of the so called American varieties of cottons in the Punjab. During these years the *desi* varieties also suffered although not to the same extent as the Americans. The symptoms of the 'disease' may be described as follows :—

The plants remain stunted, leaves begin to turn red from about the middle of October and excessive defoliation results, flowers and bolls are shed in large numbers, bolls remaining on the plants do not develop properly, remain soft and open prematurely and badly, lint is trash and seeds develop poorly.

By some investigators adverse environmental conditions such as drought, high atmospheric temperature, high soil temperature, etc., etc., have been held responsible for producing the above mentioned abnormal conditions. While others consider the white-flies the primary cause



of the disaster. Roberts and Roger Thomas hold the latter view (Agric. Jl. India, XXIV, March, 1929), and Misra and Lamba follow them (Bull. 196 Agric., Res. Inst. Pusa, 1929). The conclusions arrived at are not supported by properly investigated facts.

Misra and Lamba have studied the white-fly and have named it *Bemisia gossypiperda*. Their statement that antennæ are absent in the second instar nymph must be challenged as it is incorrect. Their list of alternative food plants is also based on insufficient data, and is probably too exhaustive.

The attack on the cotton crop starts in May and continues to increase till the end of August and then it subsides. During this time both the *desi* and American varieties are attacked equally severely. There is no defoliation and no drying of the plants. Thus at the time when the attack is at its highest the plants continue to grow and there is no apparent sign of any disease, except shining appearance and stickiness on the leaves which are due to the 'honey-dew' dropped by the insects. Later on black mould appears on this honey-dew and the lower leaves of an infested plant get covered by this black stuff. There is no spotting, discoloration, distortion, crumpling or withering of leaves, and there is no other sign of abnormal condition.

There is hardly any doubt that a plant which provides food to the numerous sucking insects cannot be normal, and the black fungus developing on the upper surface of leaves does certainly interfere with photosynthesis and checks normal respiration, as a large number of stomata are situated on this surface. All the same this interference with the functions of the leaves is not such as to produce the 'disease.'

Cases have been known where fields badly infested with white-flies have not shown the 'disease,' and conversely fields which have shown the 'disease' have been free from or very slightly attacked by the white-flies.

This year the white-fly attack was very serious right upto the end of August and yet the 'disease' has not appeared. It has been noticed that in the same fields plants which are vigorous and healthy have a larger number of white-flies on them than plants stunted and sickly. Plants grown under cages although heavily infested with white-flies do not show any of the symptoms of the 'disease.'

The disease of cotton, therefore, which brought about the failures of the American cottons in the Punjab is independent of the white-fly attack. It is of utmost importance for the future of cotton growing that this fact is recognized.

### 38.— Insects associated with South Indian Coccidæ and their economic importance.

T. V. RAMAKRISHNA AYYAR, Madras.

The paper begins with a very brief summary of such of the salient features of the Coccid insects which have a bearing on their insect associates, gives a short account of the chief characteristics of Coccid associates in general, lists the known associates of South Indian Coccidæ with their respective categories and concludes with some remarks on the significance of such associations and their economic value, with special reference to South Indian forms. The main idea of the paper, which includes only a brief summary of the author's preliminary studies in this line, is to invite the attention of other workers to the importance of the study of insect ecology—an aspect of entomology which is not only of absorbing interest to the pure scientist, but is pregnant with economic possibilities for the farmer or horticulturist.



39. The life-history of the Jasmine bug—*Antestia cruciata*.

T. K. VENKATAKRISHNAN, Hyderabad (Deccan).

*Antestia cruciata* Fb., (Fam. Pentatomidæ)—also known as "The Coffee berry bug," has been recorded as a serious pest of Coffee in Ceylon and in the Coffee areas of South India. In the plains, on the other hand, it is more familiarly known as a serious pest of Jasmine, reports of damage having been received from the districts of Bellary, Anantapore, Salem and North Arcot.

Eggs are laid in clusters of 7 to 13, generally on the lower surface of leaves. The life-cycle covers about 30 days on the average under artificial conditions in cages. The adult appears to be fairly long-lived, periods of 6 to 7 weeks having been recorded in cages. The greatest damage is done by the adult bugs, the shoots and flower-buds being punctured and caused to fade and wither. In instances of bad attack, a loss of 40% to 50% of the yield of flowers—amounting in money value roughly to a loss of Rs. 300/- to Rs. 400/- is not uncommon. As regards control methods, the 'tent-system of calcium cyanide dusting' has been found to be very effective.

40. The biological control of the fluted scale—*Icerya purchasi*—in South India.

RAO SAHIB Y. RAMACHANDRA RAO, Coimbatore.

In April, 1928, a report was received regarding serious damage by the fluted scale on a Wattle plantation at MacIvor's bund on the Nilgiris. On investigation, the scale was found already widely distributed in several places on the Nilgiri plateau, such as Fairlawns, Ketu, Wellington and Coonoor. Besides the Wattle—*Acacia decurrens*—, about 20 other plants, including the wild wattle—*Acacia dealbata*, the Broom, St. John's Wort, Gorse, Roses, and the Potato Creeper, were also found attacked. At Ketu, the infestation was evidently already three years old. It is considered almost certain that the scale must have come in through the medium of imported orchard stock. As a preliminary measure, cutting and burning of infested brooms was done at Fairlawns, in order to prevent a further spread of the pest.

The effective control of this serious pest in 1888, in California by the importation of its natural enemy—the Vedalia beetle—from the original home of the Scale—Australia, is now become a classic in the history of economic entomology. The same method has since been successfully applied in various countries which the scale has invaded, the latest example being Ceylon. The Entomologists of many of these countries—Ceylon, Java, South Africa, Rhodesia, Kenya, Egypt, Queensland, New South Wales, Victoria, South Australia, and last but not least the Imperial Bureau of Entomology, London, were approached for supplies of the Vedalia beetle. South Africa kindly responded with a consignment shipped direct to Madras in April, 1929; unfortunately, however, the contents were found dead on arrival. A second consignment shipped to Colombo by Dr. Thompson of the Farnham Royal Laboratory—obtained by him from California—was received in May, 1929. When opened out, three beetles and a dozen grubs were found alive, and these were promptly transferred to a special breeding laboratory opened at Ketu. From the scanty supply received, however, the writer is happy to state that the beetles have bred satisfactorily, so that there were 10,000 individuals in various stages in stock in August. Liberation of beetles in the various centres of infestation has now been taken in hand, and it is hoped that the scale would very soon be brought under control.



## 41. Ants and the lac insect.

P. S. NEGI, M. P. MISRA and S. N. GUPTA, Namkum.

The paper deals with eight more species of ants other than hither-to recorded associated with lac and their relation to the lac insect. Methods of control against the injurious species of ants are given.

## 42. Seasonal variations in the host-plants of the lac insect.

S. RANGANATHAN.

The paper gives the results of periodical analyses of Kusum and Ber, two of the principal host-plants of the lac insect, and an attempt is made to correlate the seasonal changes in composition with the stages in the life cycle of the lac insects parasitic on them and the annual vegetative cycles of the hosts.

Although in general the nutritive constituents in the hosts increase with the onset of spring and again during the rains in the case of Ber and a month or two later in the case of Kusum, particular importance is to be attached to the amounts of phosphorus, water-soluble solids and alcohol-soluble minerals present in the plants since the variations in these constituents synchronise with the periods of active resin production though the crop seasons are different on the two hosts.

## 43. A note on the pruning of lac hosts.

M. VENUGOPALAN and M. RANGASWAMI.

After discussing the general principles involved in all pruning operations, the paper deals with the importance of systematic and timely pruning of lac hosts for the successful propagation of lac. The dependence of methods and times of pruning on the species of host plant, age, climate and locality is indicated and the necessity of making adequate provision for proper sunlight and ventilation is emphasised.

The results of pruning experiments with three hosts like *Butea frondosa*, *Zizyphus jujuba* and *Acacia catechu* have been described and photographs taken wherever possible.

In addition, the paper describes the results of four distinct types of pruning instituted in the experimental plantation at Namkum with the view to study, (a) the effect on the vitality of the plant, (b) the number and nature of shoots produced, (c) the shape the plant would assume, at the end of a few years' systematic pruning.

## 44. A preliminary note on the nutrition of the Lac insect.

S. RANGANATHAN.

Different methods of solving the problem of the nutrition of the lac insect, some of which have already been adopted by previous workers in the field, are outlined.

Analyses have been carried out of the insects at their larval and mature stages and of two adjacent Khair plants (*Acacia catechu*) one of which was under lac crop while the other served as control.

From the results obtained it would appear that starch water-soluble-nitrogen and minerals and total phosphorus play an important part in the nutrition of the insect.



## AGRICULTURAL MYCOLOGY AND BACTERIOLOGY.

## 45. Studies on "powdery mildews" and "rusts" of cereals and the means of combating them.

K. C. MEHTA, Agra.

The writer has studied the incidence of "mildews" and "rusts" of cereals between the harvesting and the sowing periods during the last six years.

A brief account of the work on rusts of wheat was presented last year in the presidential address to the Botany section of the Indian Science Congress at Madras.

In the present paper the writer proposes to submit the proposed measures of control for a discussion which was not possible last year. Mildews and rusts of cereals have been observed growing on "self sown" plants in the hills during the critical period—May—October by the writer every year during the last six years.

The idia of mildews and the uredospores of rusts obtained from "self sown" plants showed a high percentage of viability and produced successful infection in artificial inoculations.

The occurrence of mildews and rusts under identical conditions offers a unique opportunity for control of as many as seven pests—four of wheat and three of barley.

Destruction of self-sown plants after the harvest and again before the sowing period should materially reduce the damage done by these parasites.

Suspension of the cultivation of wheat and barley for two or three years at such localities in the hills where the parasites can survive the summer should prove a very effective check and may eradicate the pests altogether.

## 46. A Bacterial stalk rot of Maize plants.

HARI HAR PRASAD.

Appearance of a bacterial stalk rot in maize round about Pusa in 1928 and 1929 has been noticed. Isolation of an organism and inoculations and cross inoculations with it prove its pathogenicity. It has the same cultural characters as an organism named *Phytomonas dissolvens* by H. R. Rosen of the Arkansas Agricultural Experiment Station who found it causing a similar disease in Arkansas. It was noticed also in some other States of America.

## 47. The use of small additions of acid for increasing the germicidal action of E.C. on bacterial spores.

C. S. RAM AYYAR, Pusa.

Tests made with the spores of various soil bacteria showed that they are not destroyed completely by E. C. (Hypochlorite) in a dilution of 1 in 500 even after 60 minutes contact in water of  $P_H$  about 7.0. If, however, a small amount of acid, viz., 0.05 per cent normal citric acid solution corresponding to 3.5 grams of citric acid per 10 litres ( $P_H$  3.9) be added to the diluting liquid before the addition of E.C., the germicidal efficiency of the latter is increased considerably and practically complete destruction of the spores takes place after 30 minutes' contact.

The practical value of these tests lies in the fact that silk house nurseries can be disinfected with greater certainty with E.C. in a dilution of 1 in 500, if to the diluting liquid a small amount of acid is added.



**AGRICULTURAL ENGINEERING.****48. Observations on the economics of threshing.****C. MAYA DAS, Cawnpore.**

1. Brief history of threshing experiments conducted and reported so far—1907 to 1929.
2. Details of recent experiment on threshing at Cawnpore.
3. Possibilities attending the introduction of modern threshing machinery driven by a motor tractor.
4. Some additional advantages of modern threshers over the country method of threshing.
5. Summary of observations.
6. Bibliography.
7. Statements I to IV of Appendix.

**49. Agricultural engineering research in India.****MASON VAUGH.**

Agricultural engineering research in India has been largely restricted to problems of water supply. In this, brilliant work has been done. The more distinctively agricultural problems have so far received little attention and the little they have had has been from men not really trained for the purpose.

Only three agencies are available for research, the agricultural engineers to Government, the engineering staffs of Agricultural Colleges and implement manufacturers. Private enterprise not connected with one of these agencies cannot be depended on for any large contribution.

The first and most fundamental problem in such research is trained personnel. Splendidly trained engineers knowing nothing of agriculture cannot be expected to make the same contribution that they could with agricultural training added. To be most effective, they must be trained not only in both subjects but in the co-ordination of them as well.

Research in agricultural engineering must go beyond testing of competing types of equipment back to the fundamental basis of the problems. We must know what we want to accomplish, have standards and methods of measuring our accomplishments and be able and willing to adopt and adapt new methods where old methods fail to give the desired results.

There are three main groups of problems to be met. The first has to do with all phases of working the soil in the preparation of seed beds, in interculture and in the handling of irrigation water in the fields. The second has to do with the problems of dressing and harvesting crops. Harvesting methods are antiquated but we are seriously handicapped in introducing western methods since conditions are so different. The problems of threshing, bhusa making, rice hulling and other crop dressings are in urgent need of attention. The third group of problems is that of farm or rural building. This should include not only the farmer's home but the whole village, his cattle and his supplies of food grains and seeds. Any one of these groups of problems is enough to demand the attention of many workers for some time.

The agencies at work in this direction are few and the workers scattered. Co-operative effort will enable us to get on with the work much faster. There are problems enough for everyone and we should not be afraid to consult others and to take their help and suggestions in planning our work.



## 50. Electricity and agriculture.

T. J. MIRCHANDANI.

This short paper is a continuation of the one on the same subject read at the last Calcutta session.

In spite of the opinion of the Royal Agricultural Commission, the author feels that the employment of electricity on the farm is not such a remote possibility—*vide*, the phenomenal development in this direction in France, Scandinavia, America, New Zealand, and even England. This is mainly to be attributed to power being available, almost at the doorstep, from lines traversing the country. These conditions, it is hoped, will be reproduced in several parts of this country by schemes of hydro-electric development, specially in the U.P., Punjab, and Madras.

A cheap and reasonably safe system of obtaining electric power from the high voltage lines is outlined and its cost worked out for existing conditions in this country. Experience gained by various countries regarding the most suitable size of motors for different duties, systems of wiring, and distribution of load, etc., is summarized and examined.

Mention is made of the methods of co-operation and hire-purchase in vogue in certain countries, and the enormous field for their application offered by this country, is pointed out.

## ANIMAL NUTRITION.

## 51. A short resumé of some aspects of the work of the nutrition section at Bangalore.

A. VISWANATHA IYER, Bangalore

The work at present is confined mostly to the nutrition of farm animals.

1. This necessitates the determination of the feeding values of coarse fodders and the more important concentrates. To obtain these values digestion experiments have been carried out with (1) rice straw, (2) ragi straw, (3) several types of hay sent from the Military Farms Department, (4) spear grass, (5) jouar, etc. This work enables us not only to obtain the feeding values of the samples under examination and their comparison, which of course is very important, but also the starch values for our fodders.

2. The work as a matter of course also necessitates the chemical and physiological examination of fodders and the metabolised products in faeces and urine. In the matter of examination of fodders a study of the several changes involved in silage and hay making which are the most commonly accepted forms of preserved fodders is also undertaken. This again brings us to the necessity of studying the best times for cutting a crop for hay or silage making with a view to utilise same in the most economical way.

## 52. Feeding experiments with young stock by the nutrition section.

T. S. KRISHNAN.

The primary objective with which growth in young stock is studied by the nutrition section of the Imperial Department of Agriculture is to get the comparative values of different fodders for growth production under various conditions.

Experiments have been conducted at various places with a number of growing animals using different fodders and animals and extremely important results have been obtained.

Besides the above another objective, though till recently considered



secondary, yet of much greater intrinsic importance, which is kept in view in all these experiments, is to determine the starch equivalents of Indian fodders, when fed to Indian cattle under local conditions.

The starch equivalents computed by European workers for different feeding stuffs are assumed and long period feeding experiments conducted and the actual growth obtained compared against the growth computed from the values assumed. The results enable the checking, correcting and establishing of accurate starch equivalents for the feeding stuffs used.

The work has only been begun and valuable data are being obtained as the result of a series of carefully planned experiments with various fodders.

### 53. Effect of maturity on the nutritive value of fodders.

A VISWANATHA IYER.

Jouar and a sample of grass supplied by the military grass farm from a uniform plot at Bolarum were the samples selected for this series of experiments. Both were examined at three stages of development, viz., young, prime and ripe.

In the case of Jouar, digestion experiments were carried out both on the freshly cut material and the same material converted into hay.

With the grass, only hay made out of it was experimented with.

From the figures obtained, it can be seen that nutritive value decreases as maturity advances. This will enable us to point out the best time for cutting a crop and of utilising same in the most economical way.

Further work on this subject is in progress.

### 54. Silage investigations at Bangalore.

T. S. KRISHNAN.

Numerous experiments conducted by the nutrition section of the Imperial Department of Agriculture on young stock have shown the advantage of using silage for growth production.

Digestion experiments with silage have repeatedly yielded a low digestion co-efficient for the protein and a high figure for the fibre.

Experiments have been started with a view to elucidating the reasons for such behaviour.

Preliminary experiments on silage have disclosed an actual loss of protein during the process of ensilage.

The depression of the protein digestibility on ensilage might reasonably be attributed to the destruction of the most easily digestible portion of the protein in the plant during the ensilage.

The high efficiency of silage must probably be due to easier availability of the silage carbohydrates.

The problem is being investigated.

The high efficiency of silage might also be due to the presence of easily assimilable minerals.

## GENERAL PAPERS.

### 55. Storage of potatoes.

N. D. VYAS.

The author deals with the experiments conducted by him on the storage of potatoes and recommends a method by which without periodical examination cultivators can keep a stock of seed potatoes for a period of six to seven months, till the next growing season, with a loss varying from 3.6 to 7.5 per cent.



The recommendations consist in harvesting potatoes early in the season, end of February being suitable for places around Pusa, drying for about a fortnight under shade, selecting the medium sized sound tubers and their storage in cinders lime mixture or charcoal in dealwood boxes.

56. The improvement of the economic relations between landlord and tenant in the United Provinces.

C. MAYA DAS, Cawnpore.

(1) Introductory: briefly reviewing literature on the subject. (2) Objects of experiment at Cawnpore. (3) Brief account of the experiment. (4) Brief summary of results so far obtained. (5) General observations. (6) Conclusions arrived at. (7) Bibliography.

57. Notes on some rats damaging crops in South India.

P. N. KRISHNA AYYAR, Madras.

It is universally recognised that there are few animals that cause, by their depredations, greater loss to man than those belonging to the group popularly known as rats. On account of their numerical strength, wide distribution, their great fecundity and adaptability to varying conditions and omnivorous feeding habits these have certainly attained unenviable notoriety all over the world. But it is only recently, comparatively speaking, that the highly important role played by them in the destruction of crops has come into prominence. The destruction caused by these to crops is undoubtedly frightful, the loss sometimes amounting to nearly fifty per cent. of the gross outturn.

There is practically very little on record regarding the species that damage crops, their habits or methods of control except the very brief and passing reference made by Fletcher in his excellent book on some South Indian Insects. Therefore this paper, so far as the writer is aware, is perhaps one of the first if not the first venture in this direction in South India.

The paper is designed to give a brief account of the biology, habits and habitations of some of the most destructive species such as the Southern mole rat *Gunomys Kok*, the soft furred mole rat *Millardia meltada*, the common Indian rat *Rattus rattus wroughtoni*, etc., which frequent and breed in cultivated areas, noted by the writer in South India, together with some noted on the nature and extent of damage caused to such valuable crops as rice, ragi and other grain crops, cotton, coconuts, tea, etc. A brief reference to the various localities where such ravages have been so far noted in South India is also made. In order to impart a sort of completeness to the subject dealt with a short account of the various control measures is also added with special reference to poison baiting and fumigation that have been given a fair trial in South India.

58. The effect of soaking maize in water before sowing.

B. S. SAWHNEY.

It was decided in July 1928 to study the effects of soaking maize in water before sowing. The advantages of soaking the seed for 8 hours and 12 hours over the unsoaked was studied. It was found that the soaking accelerated the speed of germination and soaked seed could be sown with a lesser amount of moisture in the soil than the unsoaked which was used as a control. It is interesting to note that the best results were obtained with the 8 hours soaking.

This experiment was repeated again in 1929 but this year the advan-



tages of soaking for 4, 6, 7, 8, 9, 10 and 12 hours over the control were studied. The results in 1929 were not up to our expectations due to rains just after the sowings were completed. However, they confirmed our last year's results.

This soaking of seed before sowing will enable the cultivator, who depends on the rains to do his sowing to make use of the early showers which are not usually very heavy and thus not only get a higher acreage under the crop per plough but also an increase in the field per acre due to the longer growing period of the crop.



# INDIAN SCIENCE CONGRESS.

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Seventeenth Annual Meeting,

ALLAHABAD, 1930.

ABSTRACTS OF PAPERS.

Section of Chemistry.

*President :—Prof. P. C. Mitter, M.A., Ph.D.*

CALCUTTA.

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## Section of Chemistry.

### *Abstracts.*

#### 1. Studies on Hexammine Cobaltic Sulphate.

PULIN BEHARI SARKAR *and* TARA PROSAD BARAT, Calcutta.

The luteocobaltic hydroxide  $[\text{Co}(\text{NH}_3)_6]_2(\text{OH})_3$  is a strong base and exhibits a close analogy to the alkalis by forming insoluble chloroplatinates, chloraurates, chloromercurates and fluosilicates. Like the alkali sulphates hexammine cobaltic sulphate gives insoluble sulphates with the sulphates of the rare earths. Further, hexammine cobaltic sulphate forms 3 acid salts with  $\text{H}_2\text{SO}_4$  and a double salt with  $\text{Am}_2\text{SO}_4$ . The present work was undertaken to precise the analogy of the hexammine bases with the alkalis by studying in detail the double and acid salts of the cobalt hexammine series. The double salts of  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$  with alkali sulphates are formed by crystallising a soln. of  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$  and alkali sulphates, *viz.*, the sulphates of K, Rb, Cs, Tl etc. The double salts are stable only within a narrow range of concentration. Hence the equilibrium of the ternary systems,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$  - water -  $\text{K}_2\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$  - water -  $\text{H}_2\text{SO}_4$  have been studied at  $35^\circ\text{C}$  as a result of which the formation of a double salt of  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$  with  $\text{K}_2\text{SO}_4$  and the existence of 3 acid salts with  $\text{H}_2\text{SO}_4$  have been established. Their properties and ranges of stability in soln. have also been determined.

#### 2. Analogy of diverse anions from chemical, structural and morphological points of view.

P. B. SARKAR *and* NIRMALENDUNATH RÂY, Calcutta.

#### 3. Preparation and properties of various salts of the complex ion $\text{BeF}_4^-$ .

P. B. SARKAR *and* NIRMALENDUNATH RÂY, Calcutta.

#### 4. Sulphate of Hexavalent Chromium.

H. R. IYENGAR, Bangalore.

The solubility curve of chromium trioxide in sulphuric acid indicated the existence of a compound of trioxides of chromium and sulphur (Abstr. Sc. Congress, 1928). This compound which is a brown solid has now been identified as a sulphate of hexavalent chromium. Evidence in favour of the existence of hexavalent chromium salts is discussed.

#### 5. A new complex pentacyanocobalt Compound.

PRIYADARANJAN RÂY, Calcutta.

The first instance of a pentacyano-cobalt compound was reported to the Journal of the Indian Chemical Society (Ray, 1927, 5, 3, 325). In the present paper the preparation and the properties of an entirely new bi-nuclear pentacyano-derivative have been described. The new compound has been found to be a bridge-compound with a sulphito-group and to contain a hexavalent anion. From the nature of its composition



and behaviour it is concluded to be a-sulphito-pentacyano potassium cobaltiate.

## 6. Ammoniacal Cobalt-molybdates.

PRIYADARANJAN RÂY and SAILENDRA NATH MAULIK,  
Calcutta.

The preparation and the properties of a number of complex cobalti-ammine molybdates have been described in the present paper. The compounds described are chloro-pentammine molybdate, aquo-pentammine molybdate, hydroxo-pentammine molybdate, molybdato-pentammine molybdate, aquo-nitro-tetrammine molybdate, nitro-molybdato-tetrammine cobalt, thiocyanato-pentammine molybdate and nitrato-pentammine-cobalti-molybdate.

## 7. Some derivatives of Thiosulphato-pentacyano-cobaltic acid.

PRIYADARANJAN RÂY and SAILENDRA NATH MAULIK,  
Calcutta.

The potassium salt of the thiosulphato-pentacyano-cobaltic acid has already been described by one of us (Ray, J.I.C.S. 1927, 5, 3, 325). A large number of derivatives of the same acid have now been prepared and studied. The compounds described in this paper are the sodium, ammonium, lithium, rubidium, caesium, thallium and a basic lead salt of the same acid. The isolation of the free acid has also been attempted and has met with partial success.

## 8. On the vanadates of some heavy metals.

M. B. RANE and K. KONDAIAH, Benares.

The vanadates of mercury, gold, thorium, cerium and zirconium have been prepared and their properties investigated.

Mercurous vanadate  $\text{Hg}_2\text{O} \cdot \text{V}_2\text{O}_5$  is a reddish brown to orange compound when pure; it however varies in composition on account of oxidation, when the colour of the compound also darkens. Mercuric vanadate  $2\text{HgO} \cdot \text{V}_2\text{O}_5$  is a bright yellow crystalline compound (slightly fluorescent) readily obtained by the action of ammonium meta vanadate on an aqueous solution of mercuric nitrate. On heating it gets decomposed into mercury and  $\text{V}_2\text{O}_5$ .

Gold chloride forms a compound with ammonium vanadate which is bright golden yellow when freshly made and possesses the composition  $\text{Au}_2\text{O}_3 \cdot (\text{NH}_4)_2\text{O} \cdot 2\text{V}_2\text{O}_5$ ; on heating, the compound first darkens in colour and then decomposes with a sharp sound giving out ammonia; it is unstable even at ordinary temperatures. Metallic gold, when left in contact with a solution of ammonium metavanadate acidified with  $\text{HCl}$ , gradually goes into solution.

$\text{ThO}_2 \cdot \text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$  can be obtained by the action of ammonium meta vanadate on thorium chloride. The bright yellow compound when heated, loses water, turns olive green and finally decomposes into  $\text{ThO}_2$  and  $\text{V}_2\text{O}_5$ . Thorium vanadate made from thorium nitrate and ammonium metavanadate (in hot solutions), on standing or being heated, appears to be mixed with thorium hydroxide.

Ceric vanadate, a golden yellow compound obtained from ceric sulphate and ammonium metavanadate, correspond to the formula  $3\text{CeO}_2 \cdot \text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ . It loses water on gently heating and decomposes into  $\text{CeO}_2$  and  $\text{V}_2\text{O}_5$  at higher temperatures. Zirconium vanadate can be



obtained as a highly gelatinous, bright yellow precipitate when a solution of zirconium nitrate is treated with ammonium metavanadate.

### 9. On the composition of Prussian blue and Turnbull's blue.

ABANI KUMAR BHATTACHARYA, Bareilly.

The composition of Prussian blue and Turnbull's blue were determined with varying concentrations of  $\text{FeCl}_3$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ , and  $\text{FeSO}_4$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  and the following results were obtained:—

PRUSSIAN BLUE.		TURNBULL'S BLUE.	
Ratio of concentrations of $\text{FeCl}_3 : \text{K}_4\text{Fe}(\text{CN})_6$ .	Ratio of Fe : CN.	Ratio of concentrations of $\text{FeSO}_4 : \text{K}_3\text{Fe}(\text{CN})_6$ .	Ratio of Fe : CN.
1 : 1	1 : 2.50	1 : 1	1 : 2.50
1 : $\frac{3}{2}$	1 : 2.67	1 : $\frac{3}{2}$	1 : 2.53
$\frac{3}{2} : 1$	1 : 2.35	$\frac{3}{2} : 1$	1 : 2.50

The ratio of Fe : CN in Prussian blue  $\text{Fe}_4''' [\text{Fe}(\text{CN})_6]_3'''$  is 1 : 2.57 and that in Turnbull's blue  $\text{Fe}_3'' [\text{Fe}(\text{CN})_6]_3''$  it is 1 : 2.40.

The above results show that (a) the ratio of Fe : CN is the same when the concentrations of the reactants of Prussian blue and Turnbull's blue are in equivalent proportions, and (b) the compositions of Prussian blue and Turnbull's blue are variable with the concentrations of the reactants.

From (a) it can be suggested that the ferric portion of Prussian blue partially oxidises the ferrocyanide portion, whilst in the case of Turnbull's blue the ferrous portion partially reduces the ferricyanide portion. Hence, it is probable that an intermediate compound results having a formula in which the ratio of Fe : CN is less than 1 : 2.57, but greater than 1 : 2.40.

The variations in the composition of Prussian blue on adding excess of either  $\text{FeCl}_3$  or  $\text{K}_4\text{Fe}(\text{CN})_6$  are due to the adsorption of both  $\text{Fe}''$  and  $\text{Fe}(\text{CN})_6'''$  ions. With Turnbull's blue no remarkable change in the composition is observed with varying concentrations of either  $\text{FeSO}_4$  or  $\text{K}_3\text{Fe}(\text{CN})_6$  as the adsorption of the  $\text{Fe}''$  or  $\text{Fe}(\text{CN})_6'''$  is very small.

### 10. The Chemistry of Nickel Oxide in Mond's process.

MATA PRASAD and M. G. TENDULKAR, Bombay.

In the manufacture of nickel by Mond's process, the action of sulphuric acid on the matte obtained by roasting the ore, containing greater per cent of copper than nickel, removes nearly all the copper but the loss of nickel does not amount to more than one per cent. Oxides of nickel dissolve very readily in acids and from the positions of nickel and copper in the electro-chemical series of elements it is expected that nickel will go in solution more readily than copper.

The distribution ratio of  $\text{Ni}_2\text{O}_3$  and  $\text{CuO}$  and of  $\text{NiO}$  and  $\text{CuO}$  in sulphuric acid has been measured and it has been found that in the former case more nickel oxide goes in solution than copper oxide. But in the latter case the amount of nickel oxide going in solution is much smaller than copper oxide and this amount goes on decreasing as the temperature at which the nickel oxide is prepared is raised; the sample of  $\text{NiO}$  prepared at  $1000^\circ\text{C}$  does not at all go in solution. Such an oxide has been prepared by heating nickel nitrate or nickel sulphate or nickel hydroxide to  $1000^\circ\text{C}$ . The colour of  $\text{NiO}$  also changes from black—grey—green as the temperature of preparation is changed from  $400^\circ\text{C}$ — $1000^\circ\text{C}$ . The solubility of the oxide in sulphuric acid regularly diminishes: the



density increases and the specific resistance and the magnetic susceptibility also increases.

11. Estimation of Potassium, Rubidium and Cæsium gravimetrically by Zirconium Sulphate Method.

N. A. YAJNIK and G. L. TANDON, Lahore.

Gravimetric estimations of potassium, rubidium and cæsium have been carried out by the use of zirconium sulphate, which forms double sulphates with the sulphates of the above elements. The results obtained by this method are as accurate as those obtained by other well-known methods. Besides this it is found to have a decided advantage over the other methods in the fact that the presence of ammonium ions has no effect on the accuracy of the method.

12. A new formula for fluoremetry.

K. S. G. DOSS, Bangalore.

For the micro-analysis of fluorescent substances L. J. Desha (J.A.C.S., 42, 1363) has suggested the use of Kober's nephelometric formula. This formula is purely empirical. The present paper deals with a new formula which agrees well with experimental results. In this formula the fluorescent intensity is calculated from the incident intensity by putting Perrin's idea of protective action into a quantitative form. Correction for absorption is made on the basis of Lambert and Beer's law. The final intensity is thus expressed as a function of the depth of the solution and the concentration of fluorescent substance. The formula is specially applicable to cases in which the duration of the critical state is small (e.g., alkaline solution of fluorescein).

13. Interaction between nitrosyl chloride and ammonia.

G. SAMBAMURTI and N. L. NARASIMHAM, Rajahmundry.

Ammonia and nitrosyl chloride produce an amide,  $\text{NO}\cdot\text{NH}_2$ .

14. The Contact Sulphuric Acid Process.

K. W. KHUBOHANDANI.

Experiments have been conducted to test the efficiency of certain catalysts such as vanadium pentoxide and silver vanadate recently described in patent literature, for converting sulphur dioxide into trioxide. The effect of varying conditions has been studied and good results obtained in several cases.

15. The influence of adjacent groups on the stability of the double bond in unsaturated compounds. Part I. The Benzalmalonic Acids.

SARBBANI SAHAY GUHA-SIROAR and DEBENDRA NATH DATTA, Dacca.

The object of the present series of investigations is to find by quantitative experiments a comparative measure of the ease with which the double bond in analogous series of carbon compounds is either ruptured or converted into a single bond, with a view to finding the influence of vicinal groups on such reactions. The carbon-to-carbon double bonds in (a) some substituted benzalmalonic acids, (b) some coumarin derivatives, and (c) some substituted cinnamic acids are now under investigation. The present paper refers to the first series (a).



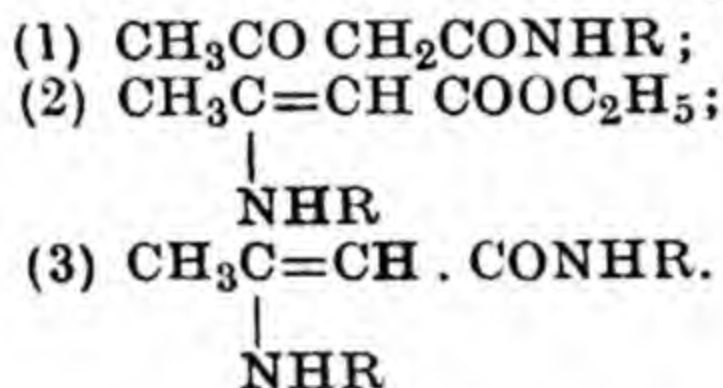
The fission of the double bond in these compounds has been effected by warming in a thermostat an N/10 solution of the neutral potassium salt of the acids with the equivalent amount of an N/10 solution of phenylhydrazine hydrochloride or acetate, at the end of definite intervals taking out the samples and filtering off the aldehyde-phenylhdrazone in a Gooch crucible and drying and weighing its amount. The velocity of the double decomposition has been found to follow the bimolecular law and in 14 cases out of 16 compounds so far studied satisfactory constants have been obtained. The formation of an oily phenylhydrazone in the remaining 2 cases rendered the method ineffective.

The work is being continued. The following are the tentative conclusions. Ortho-substituents increase the stability of the molecule no doubt by steric hindrance. Meta substituents have less influence. Para-substituents have the least effect. Of the groups chloro—, methoxy—, hydroxy—, methyl—, and nitro—, the last has the most powerful effect in stabilising the molecule.

## 16. Synthesis of quinoline derivatives.

G. V. JADHAV, Bombay.

When ethyl acetoacetate is condensed with aromatic amines the possible reaction products can be divided into three groups:—



A substance in group (1) or (2), (a) when heated alone gives the corresponding substance in group (3), (b) when heated with sulphuric acid can give a quinoline derivative.

Knorr prepared 2-oxyquinoline derivatives starting with the condensation products of ethyl acetoacetate and aniline (and its homologues). (*Ber.*, 1884, 17, 540). Later Conrad and Limpach obtained corresponding 4-oxy-compounds. (*Ber.*, 1888, 21, 521). But no attempt was made to see the effect, on the synthesis, of substituents in the nucleus of the amine.

The following amines have been used:

*o*, *m*, and *p* chloranilines; *m* and *p* nitranilines;  
*p* anisidine and *p* phenetidine.

*m* and *p*-chloraniline products give quinoline derivatives:

*m* and *p*-nitraniline products are decomposed and the original amines are obtained.

## 17. Isomerisation of benzylidene compounds.

H. S. JOIS and B. L. MANJUNATH, Bangalore.

When benzaldehyde is condensed with 4:6-dianilino-1:3-diaminobenzene, the corresponding dibenzylidene compound is formed (bright red prisms, m.p. 165–166°). This substance is easily hydrolysed by dilute acids. However, if it is heated with solvents a colourless isomer is obtained (m.p. 281–282°). The new compound exhibits fluorescence and is acted upon by dilute acids. It is probably the dibenzyl derivative of dihydroflourindene.

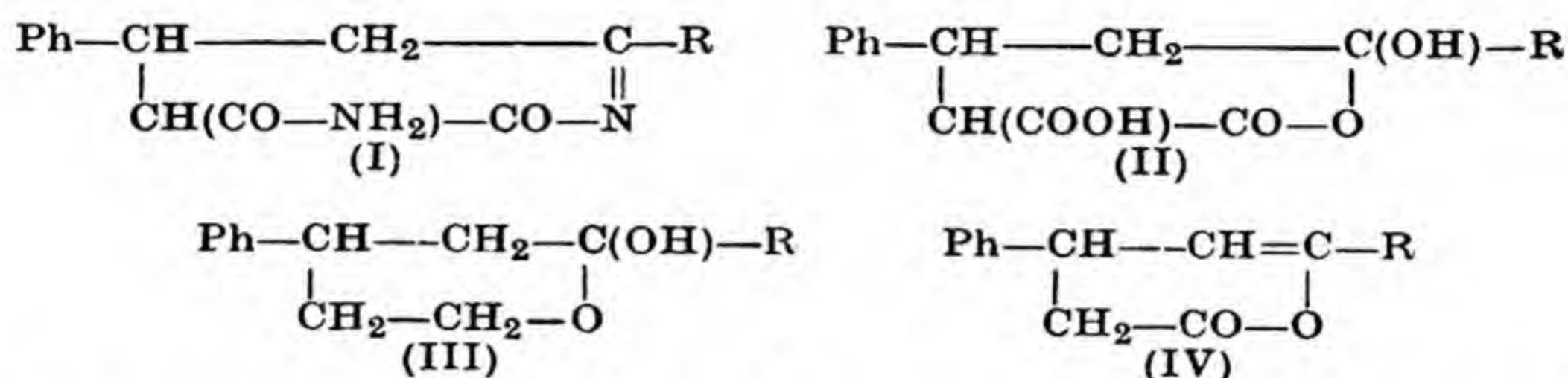
The nature of this kind of isomeric transformation is being investigated further with similar simple substances.



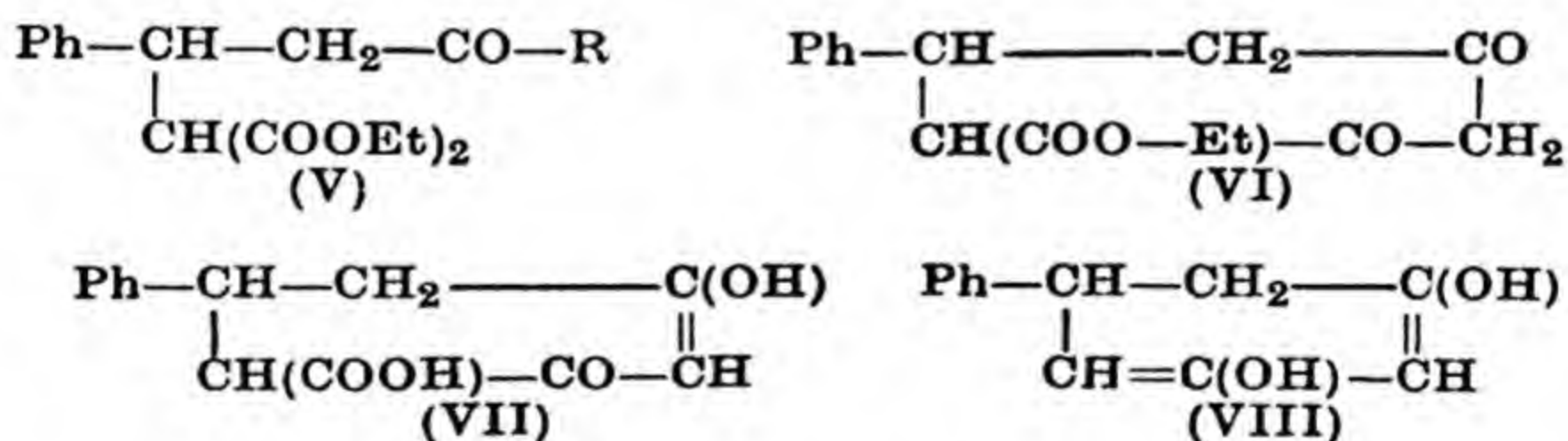
## 18. Reactivity of Conjugated Double-bonded Systems.

CHITTARANJAN BARAT, Calcutta.

In continuation of an earlier work, (Proc. Ind. Sci. Congress, 1928) arylidene ketones have been condensed with malonamide, when the methylene group of the latter reacts with the ethylenic bond of the ketone followed by ring closure, giving a tetrahydro-pyridone derivative (I), which retains its closed-ring constitution when subjected to alkaline hydrolysis, but forms a lactol acid (II) when hydrolysed by acids. This, on heating gives the lactol (III) by loss of  $\text{CO}_2$ , which again on dehydration is converted into the unsaturated lactone (IV); on boiling with aqueous alkali (IV) is reconverted into the original lactol (III).



The constitution of these latter compounds has been established by obtaining identical compounds by hydrolysing the condensation products (V) between the corresponding ketones and malonic ester; when however,  $\text{R}=\text{CH}_3$ , dihydroresorcinol derivatives, (VI, VII, and VIII) are obtained by the loss of a molecule of ethyl alcohol, instead of the lactol compounds.

19. A study of the interaction between thionyl chloride and substances containing the reactive methylene ( $-\text{CH}_2-$ ) group. Part I.—Formation of Sulphoxides.

K. G. NAIK, R. D. DESAI and M. M. PAREKH, Baroda.

The following substances were examined :—

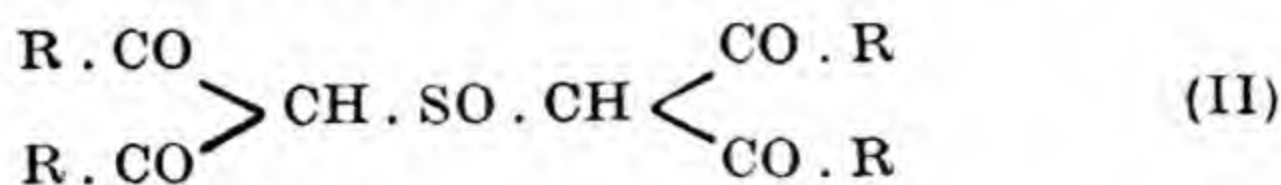
(1) Malondiphenylamide, (2) malondi-*o*-tolylamide, (3) malondi-*m*-tolylamide, (4) malondi-*p*-tolylamide, (5) malondi-(1:4:5)xylidide, (6) malondi- $\alpha$ -naphthylamide, (7) malondi- $\beta$ -naphthylamide, (8) malonmono-phenylamide, (9) malonmono-*o*-tolylamide, (10) malonmono-*m*-tolylamide, (11) malonmono-*p*-tolylamide, (12) malonmono- $\alpha$ -naphthylamide, (13) malonmono- $\beta$ -naphthylamide, (14) malondimethylphenylamide, (15) malon-*p*-tolylamate, (16) malon-*o*-tolylamate, (17) malondimethylamide, (18) malondiethylamide, (19) malondipropylamide, (20 and 21) malondibutylamide (normal and *iso*), (22) malonamide, and the amides of methylmalonic acid.

Of the above (1) to (16) gave sulphoxides of the general formula :





In the case of (17) and (18) substances of the general formula



were obtained; (22) did not react at all, while in all the other cases, though there was a vigorous reaction, it was not possible to get the end-products, owing to the very unstable nature of these compounds.

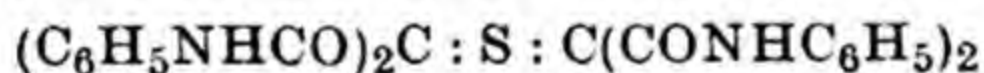
The sulfoxides having the constitution (I) are very unstable, and are decomposed even by moist air, while those having the constitution represented by (II) are fairly stable.

The reactivity of the hydrogen atoms of a methylene group is influenced in much the same way by the adjacent groupings as was observed by Naik and his collaborators.

## 20. A study of the interaction between thionyl chloride and substances containing the reactive methylene ( $-\text{CH}_2-$ ) group. Part II.—Conversion of Sulphoxides into Sulphides.

K. G. NAIK and M. M. PAREKH, Baroda.

It was observed during the action of thionyl chloride on malondiphenylamide, that when the action of  $\text{SOCl}_2$  is continued for four hours a compound having the constitution,



is obtained. This action has been studied in the case of the other substituted amides. They are—

(1) Malondiphenylamide, (2) malondi *o*-tolylamide, (3) malondi-*m*-tolylamide, (4) malondi *p*-tolylamide, (5) malondi- $\alpha$ -naphthylamide, (6) malondi- $\beta$ -naphthylamide, (7) malonmonophenylamide, (8) malonmono-*m*-tolylamide.

All these give rise to the sulphides of the general formula,  $[(\text{RNHCO})_2\text{C}]_2\text{S}$ ; in the case of (5) and (6), however, besides these sulphides, byproducts containing no sulphur and having melting points higher than those of the original amides were obtained, which are still under investigation.

An examination of the reaction in the presence of (a) dry hydrochloric acid gas and (b) iodine, as catalysts, shows that the conversion of the sulfoxides into sulphides is due to the catalytic action of thionyl chloride.

## 21. Interaction of iodine monochloride with substances containing the reactive methylene ( $-\text{CH}_2-$ ) group.

K. G. NAIK and C. C. SHAH, Baroda.

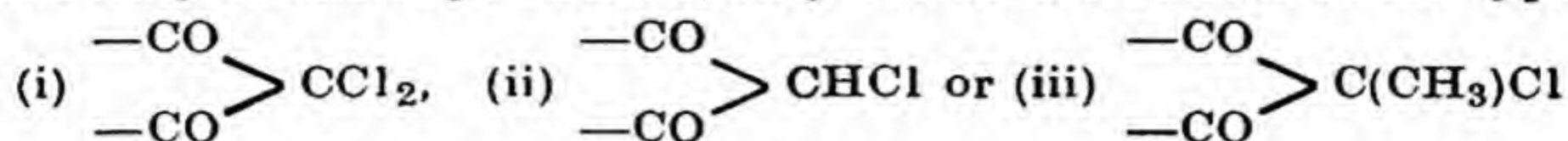
This work was undertaken to prepare the iodo-derivatives of the substituted malonamides. The reagent employed was iodine monochloride, and its interaction with the following compounds was studied:—

(1) Malondipropylamide, (2) malondiheptylamide, (3) malonamide, (4) malondibenzylamide, (5) malondiphenylamide, (6) malondi-*o*-tolylamide, (7) malondi-*p*-tolylamide, (8) malondimethylphenylamide, (9) malondi- $\alpha$ -naphthylamide, (10) malon monophenylamide, (11) malonmono-

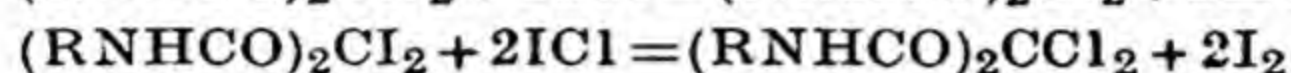
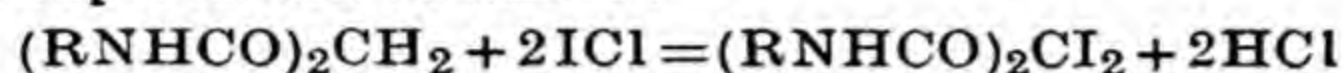


*p*-tolylamide, (12) methylmalondiphenylamide, (13) methylmalondi-*o*-tolylamide.

Contrary to the expectations, only chloro-derivatives of the type,



were obtained as the only reaction products. In some cases chlorination of the nucleus also takes place. This formation of the chloro-compounds has been explained as being due to the very unstable nature of such iodo-compounds (cf. Willstätter, *Ber.* 1902, 35, 1377). The course of the reaction is represented as under:—



## 22. Studies in the Ligno-cellulose Group. Part III.—Saccharification of *Excoccaria Agallocha* and its acetylation.

H. K. SEN, PATITPABAN PAL, and SUSHIL KUMAR BOSE,  
Calcutta.

In order to obtain a better insight into the nature of combination, if any, between lignin and cellulose and also into whether the cellulose complex itself is uniform, following acids were used for saccharification: formic, acetic, monochloroacetic, trichloroacetic, benzenesulphonic, sulphuric, and hydrochloric acids.

*Excoccaria* of comparatively mature growth has the following approximate composition:—

Moisture	..	..	..	16.48%
Soluble in cold water	..	..	..	1.03%
Soluble in hot water	..	..	..	2.87%
Fat, wax, resin, etc.	..	..	..	1.06%
Soluble in 1% caustic soda solution	..	..	..	11.91%
Cellulose by Cross and Bevan's method	..	..	..	43.18%
Cellulose by chlorine peroxide method	..	..	..	55.79%
Lignin	..	..	..	31.51%
Pentosan	..	..	..	16.28%
Ash	..	..	..	2.43%

The destruction of hemicellulose in the isolation of cellulose by Cross and Bevan's method, and its retention in the chlorine peroxide method is shown in the table below:—

(Composition of cellulose by Cross and Bevan's method).

$\alpha$ -Cellulose	..	72.73%
Hemicellulose	..	27.27%
Pentosan	..	7.26%

(Composition of cellulose by chlorine peroxide method).

$\alpha$ -Cellulose	..	55.77%
Hemicellulose	..	44.23%
Pentosan	..	25.72%

Acetylation by boiling with acetic anhydride usually gave an acetate insoluble in acetone or chloroform, corresponding to a diacetate, whilst acetic acid—acetic anhydride—sulphuric acid mixture invariably gave a soluble triacetate unmixed with lignin. It is conjectured that the sulphuric acid acts far more drastically than is ordinarily believed, and causes the elimination of lignin from the complex, giving rise at the same time to a hydroxyl group which is simultaneously acetylated.

Saccharification by various acids at different dilutions and under various pressures leads to the conclusion that a sort of equilibrium is established between the cellulose and the sugar, which latter is decom-



posed in contact with the acid under the condition of digestion. A comparatively young tree gave a much higher percentage of fermentable sugar giving frequently as high as 40 gallons of spirit per ton of saw dust. This would seem to indicate the need for selecting the age of a tree for technical utilisation as a source for power alcohol, provided of course the timber quality does not materially suffer thereby.

The hydrolysis of saw dust by organic acids of various strengths points to the probable existence of differently polymerised bundles.

### 23. 3-Sulphosalicylic acid.

N. W. HIRVE, Bombay.

3-Sulphosalicylic acid has been obtained from 3-sulpho-5-nitrosalicylic acid by removal of the  $-\text{NO}_2$  group in the usual way (reduction, diazotisation and reduction).

3-Sulphosalicylic acid, which is new, is distinct from the well known 5-sulphosalicylic acid in respect of various properties, e.g., melting point and water of crystallisation in the acids and their salts.

The constitution of 3-sulphosalicylic acid has been proved (a) by nitrating it, when the original 5-nitro-3-sulphosalicylic acid was obtained; (b) by bromination, when 3-sulpho-5-bromosalicylic acid was obtained which on distillation with super-heated steam gave 5-bromosalicylic acid.

### 24. 4-Sulphosalicylic acid.

N. W. HIRVE and M. R. JAMBHEKAR, Bombay.

4-Sulphosalicylic acid may conceivably be synthesised in two different ways from (a) *o*-nitrotoluene and (b) *o*-cresol.

(a) *o*-Nitrotoluene when sulphonated with fuming sulphuric acid gives 2-nitrotoluene-*p*-sulphonic acid; this on oxidation gives 2-nitro-4-sulphobenzoic acid. 4-Sulphosalicylic acid has been obtained from the above acid on substituting  $-\text{NO}_2$  by  $-\text{OH}$  in the usual way.

(b) *o*-Cresol on sulphonation with fuming sulphuric acid is said to give 2-hydroxy-*p*-toluene sulphonic acid, which on further oxidation should give 4-sulphosalicylic acid.

### 25. 3-Nitro-2-hydroxy-4-methoxybenzaldehyde and its derivatives.

M. SESHAIYENGAR and K. SANTHANAM, Bangalore

The nitration of 2-hydroxy-4-methoxybenzaldehyde gives a very small yield of the 3-nitro-derivative (I.Sc. Congress, 1925). The best method to obtain a greater yield has been worked out. The methyl ether of the 3-nitro-aldehyde melts at  $85-86^\circ$  and its ethyl ether at  $57^\circ$ .

On treatment with bromine it gave a mono-bromo-derivative melting at  $126^\circ$  identical with one of the products obtained by nitrating 5-bromo-2-hydroxy-4-methoxybenzaldehyde and a dibromo-compound melting at  $127-128^\circ$  identical with the dibromo-derivative obtained by brominating 6-nitro-resorcylic-3-methyl-ether. On reduction with sodium hydrosulphite and applying Sandmeyer's reaction a bromo-derivative melting at  $108-110^\circ$  was obtained.

The paper deals with the constitution and reactions of the derivatives so obtained.

### 26. Molecular rearrangement during bromination.

M. SESHAIYENGAR and K. SANTHANAM, Bangalore.

In continuation of a previous paper (Ind. Sc. Congress, 1929) it is noticed that when 3-nitro-2-hydroxy-4-methoxybenzaldehyde is bromi-



nated it gives rise to a product identical with the dibromo-derivative obtained by brominating the 5-nitro-isomeride. The experiments conducted so far indicate definitely that the rearrangement does occur during bromination. Instances of exchangeability of nitro-groups by halogen atoms are known (Monatsh., 1925, 46, 91) as also the substitution of the aldehyde groups by nitro groups; replacement of halogens by nitro-groups is also common. The paper deals with the discussion whether the molecular rearrangement is an effect of two successive substitutions, or whether it is due to a wandering of the nitro-group.

## 27. Condensation of acetone dicarboxylic acid with phenols and phenolic ethers.

D. B. LIMAYE and V. M. DIXIT, Poona.

During the synthesis of coumaryl-4-acetic acid (J. Indian Chem. Soc. 1927 4, 154 by one of us (D.B.L.) the formation of a by-product was observed which was thought to belong to the *para* series. This observation has been confirmed, a modified process giving greater yield worked out, and the reaction extended to phenolic ethers. Thus phenol gives a dicarboxylic acid ( $C_{11}H_{10}O_5$ , m.p.  $184^\circ$  decomp.), the methyl ether of which (m.p.  $176^\circ$  decomp.) gives on oxidation, anisic acid, proving condensation in the *para* position. Anisol gives a methylated dicarboxylic acid identical with the above ether. *o*-Cresol methyl ether also gives a similar dicarboxylic acid.

## 28. On Asymmetric Synthesis.

P. NEOGI and MD. ISAQUE, Calcutta.

The synthetic preparation of both *d*- and *l*- modifications of  $\alpha$ - $\beta$ -dibromo-cinnamic acid by the bromination of cinnamic acid in the presence of alkaloids has been attempted.

## 29. On Asymmetric Synthesis of Organic Sulphur Compounds.

B. K. MENON and P. C. GUHA, Bangalore.

Smiles in 1905 attempted this synthesis by the addition of *l*-menthyl brom acetate to methyl ethyl sulphide and subsequent removal of the menthyl group by hydrolysis. The resulting thetine was however found to be inactive. It was expected that the chances of racemisation due to free rotation of a thetine obtained from a closed ring sulphide are likely to be less due to the spiran structure of the compound. The hydrolysis of *l*-menthyl ester of methyl tetra methylene thetine bromide with concentrated hydrochloric acid resulted in an inactive compound. Further work in this line using alkaloidal salts of unsymmetrical thetine bromides in place of *l*-menthyl ester of thetine bromides is in progress.

## 30. A new method of conversion of coumarins to *ortho*-coumaric acids.

R. N. SEN and D. CHAKRAVARTI, Calcutta.

A new method of effecting readily the conversion of substituted coumarins into *ortho*-coumaric acids by means of (a) yellow mercuric



oxide, and (b) mercuric acetate is described. Coumarins, having negative substituents in the 6 position (such as the nitro-, aldehydo-, iodo-, dichloro (6:8)-, di-bromo (6:8)-coumarins are quantitatively converted to *ortho*-coumaric acids when their dilute alkaline solution is boiled for half an hour with a small quantity of yellow mercuric oxide.

Similar conversion of 6-nitro-, 6:8-dichloro-, and 6:8-dibromo-coumarins to the corresponding *ortho*-coumaric acids also takes place very readily with quantitative yields by adding an aqueous solution of mercuric acetate to a caustic soda solution of the coumarins neutralised with acetic acid in the cold, dissolving the precipitate in cold caustic soda and reprecipitating with dilute hydrochloric acid. In the case of coumarin, however, a dimercury derivative of *ortho*-coumaric acid is first formed which when boiled with hydrochloric acid, gives a quantitative yield of *ortho*-coumaric acid.

### 31. On mercuration of coumarins.

R. N. SEN and D. CHAKRAVARTI, Calcutta.

6-Chloro-mercuricoumarin and 6:8-dichloro-mercuri-coumarin have been obtained by boiling a dilute alkaline solution of coumarin with yellow mercuric oxide for three to four hours and then acidifying with dilute hydrochloric acid in the cold in the same way as was done by White (J.A.C.S. 1920, 42, 2355) for mercurating the phthaleins. The behaviour of these compounds towards sodium carbonate and bicarbonate solutions and caustic alkalis is exactly similar to that of coumarin itself. 4-7-Dimethyl-6:8-dichloro-mercuri-coumarin has been obtained from 4:7-dimethyl-coumarin in the same manner. 6-Substituted coumarins are not thus mercurated but are converted to the corresponding *ortho*-coumaric acids.

A diacetoxy-mercury derivative of *ortho*-coumaric acid is obtained by neutralising an alkaline solution of coumarin with acetic acid and adding an aqueous solution of mercuric acetate to the solution of the coumarinic acid. A quantitative yield of *ortho*-coumaric acid is obtained from this dimercury derivative by treatment with moderately dilute hydrochloric acid. The identical dimercury derivative is also obtained when an alkaline solution of *ortho*-coumaric acid is boiled with yellow mercuric oxide and acidified with acetic acid.

By similar treatment with mercuric acetate  $\beta$ -methyl-umbelliferone gives 4-methyl-7-hydroxy-6:8-diacetoxy-mercuri-coumarin, while  $\beta$ -methyl-daphnetin gives a dimercury derivative in which the mercury atoms are attached to the oxygen.

N-mercuri-amino-coumarin is obtained when an acetic acid solution of 6-amino-coumarin is warmed to 60-70° with an aqueous solution of mercuric acetate.

### 32. Mercuration of compounds containing the reactive methylene ( $\text{CH}_2-$ ) group.

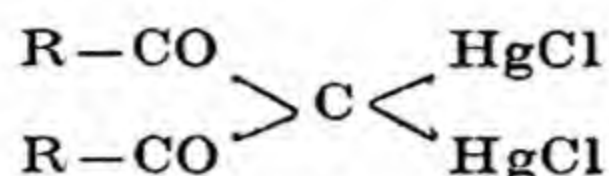
K. G. NAIK and C. C. SHAH, Baroda.

The mercuration was carried out by means of mercuric chloride in presence of sodium bicarbonate and glycerol (Neogi and Chatterji, J.I.C.S. 1928, 5, 221). The following compounds were mercurated:—

(1) Malonamide, (2) malondimethylamide, (3) malondiethylamide, (4) malondipropylamide, (5) malondibutylamide, (6) malondi-*iso*-butylamide, (7) malondiamylamide, (8) malondi-*iso*-amylamide, (9) malondiheptylamide, and (10) malonic ester.



These gave rise to mercurated products having the general formula :



The action of (a) concentrated hydrochloric acid, (b) aqueous and alcoholic potassium iodide, (c) hydrogen sulphide and (d) sodium thio-sephate on  $(\text{ClHg})_2 \text{C} : (\text{COOC}_2\text{H}_5)_2$ , dichloromercuri-malonic ethyl ester, and of (a) alcoholic potassium iodide, and (b) concentrated hydrochloric acid on dichloromercuri-malondiheptylamide has been studied; it was found that they behave generally as organo-mercury compounds having mercury attached to a carbon atom in  $\alpha$ -position to a keto-group.

### 33. Condensation of *m*-Cresotic Acid with Chloral.

N. M. SHAH and R. L. ALIMCHANDANI, Dharwar.

The condensation of *m*-cresotic acid with chloral in presence of sulphuric acid gives a complex mixture of substances from which 3 products have been isolated: 3-hydroxy-6- $\alpha$ -hydroxy- $\beta\beta\beta$ -trichloroethyl-*p*-toluic acid (A),  $\omega\omega$ -dichloro-5-carboxy-2-methyl-4-hydroxyacetophenone (B), and a third substance which is under investigation. (A) on treatment with zinc and acetic acid gives 3-hydroxy-6 $\beta\beta$ -dichloroethyl-*p*-toluic acid (C), the methyl ether of which was previously obtained by Meldrum and Alimchandani (J.I.C.S., 1925, 2, 4). (B) by similar treatment undergoes a change in which the group  $-\text{CO}.\text{CHCl}_2$  becomes  $-\text{CH}_2.\text{CH}_3$ . On hydrolysis (A) yields a substituted mandelic acid while on oxidation it gives  $\alpha$ -coccinic acid (Meldrum and Alimchandani, J.I.C.S., 1929, 6, 253). (C) on treatment with sulphuric acid undergoes a change in which the group  $-\text{CH}_2.\text{CHCl}_2$  by hydrolysis and oxidation becomes  $-\text{CH}_2.\text{CO}_2\text{H}$ .

When, however, the solution of *m*-cresotic acid and chloral in sulphuric acid is saturated with hydrochloric acid, the main product of the reaction is 3-hydroxy-6- $\alpha\beta\beta\beta$ -tetrachloro-*p*-toluic acid with small quantities of two other substances which are under investigation.

### 34. Formation of phthalides from substituted *m*-oxybenzoic acids.

P. C. MITTER and P. K. PAUL, Calcutta.

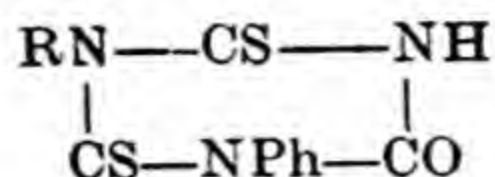
Edwards, Perkin and Stoyale have prepared meconines by the action of formaldehyde and hydrochloric acid on veratric and *o*-veratric acids (J.C.S. 1925, 197). Later, Ray and Robinson (J.C.S. 1925, 1620) have found that the yield of meconines is improved by using acetic acid as solvent. In repeating the experiments with gallic and myristic acids it was found that while the first method gives phthalides Perkin and Stoyale's modification gives chloro-methyl phthalides, which can also be prepared by the action of formaldehyde and hydrochloric acid on the acetic acid solution of pathalides prepared by the first method.

### 35. Extension of Michael's Reaction. Part II.—Action of Urethane on Mustard oils and *iso*Cyanates.

T. N. GHOSH and P. C. GUHA, Bangalore.

Urethane reacts equally well with mustard oils and *isocyanates* to form addition compounds of the type  $\text{RNH}-\text{CS}-\text{NH}-\text{COOEt}$  (type I) and  $\text{RNH}-\text{CO}-\text{NH}-\text{COOEt}$  (type II). In the case of the aromatic mustard oils the carbethoxy-thioureas (type I) cannot be isolated because as soon as they are formed they yield compounds like type (III) by react-





ing further with mustard oils. This explanation has been confirmed by preparing identical compounds (of type III) by allowing carbethoxy thioureas (prepared by Doran's method) to react with mustard oils. Carbethoxyureas (type II) however, show no tendency to react with mustard oils and isocyanates.

### 36. Isomeric Iminothiobiazolones and Iminothiolthiobiazoles.

S. L. JANNIAH and P. C. GUHA, Bangalore.

The isomerism of hydrazodithiodicarbonamide and the substituted hydrazide has been further established by a study of their absorption spectra and other physical properties. Some new ring compounds have been obtained by the action of hydrochloric acid on the hydrazides and their relation to endoxy-aminothiobiazole has also been elucidated from their absorption spectra curves.

### 37. $\alpha$ -Oxy- $\beta$ -phenylthiocarbamide.

P. P. PATEL and P. C. GUHA, Bangalore.

Though Fisher (Ber., 22, 1935), Kall. (Ann., 263, 260) and Voltmer (Ber., 24, 380) succeeded in preparing  $\alpha$ -oxy- $\beta$ -phenylthiocarbamide after the failure of Schiff (Ber., 9, 574) in the same attempt, they got low yields and their procedure was tedious. A quantitative yield of the pure crystalline compound has now been obtained easily, by modifying the older methods.

By boiling with alcohol and water, the compound is converted into two isomeric triphenylisomelamines and not into a furodiazole derivative as mentioned in Indian Science Congress Abstract (1928, p. 157). Hot dilute HCl converts it into phenylcarbamide and sulphur. The compound gets decomposed into the same products even when kept in vacuum over sulphuric acid. On treating a cold aqueous alkaline solution with iodine it decomposes into phenylisocyanide and sulphur.

### 38. Mixed Hydrazodithiodicarbonamides and their Ring-Closure.

P. P. PATEL and G. C. CHAKRAVARTI, Bangalore.

Several mixed hydrazodithiodicarbonamides have been obtained by the action of different mustard oils upon 4-substituted thiosemicarbazides, viz., 1-phenyl-6-*o*-tolyl, 1-phenyl-6-*m*-tolyl, 1-phenyl-6-*m*-xylyl, 1-*o*-tolyl-6-*m*-xylyl, 1-*m*-tolyl-6-*m*-xylyl and 1-*o*-tolyl-6-*m*-tolyl—hydrozodithiodicarbonamides.

2:5-Phenyl-*o*-tolyl, 2:5-phenyl-*m*-tolyl, 2:5-phenyl-*m*-xylyl, 2:5-*o*-tolyl-*m*-xylyl, 2:5-*m*-tolyl-*m*-xylyl and 2:5-*o*-tolyl-*m*-tolyl—diimino-2:3:4:5-tetrahydro-1:3:4-thiodiazoles obtained by oxidation by iodine from the above mixed hydrazo compounds, melt respectively at 200°, 216°, 189°, 205°, 190° and 190°.

Diacetyl derivatives of these thiodiazoles melt respectively at 223°, 177°, 120°, 224°, 263° and 231°.

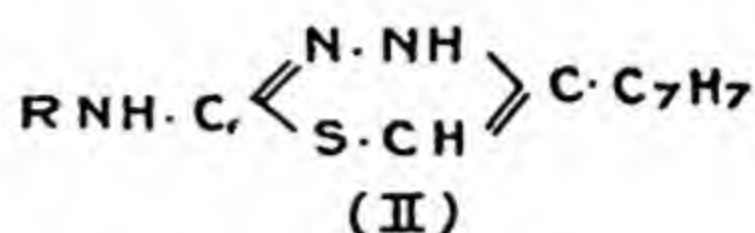
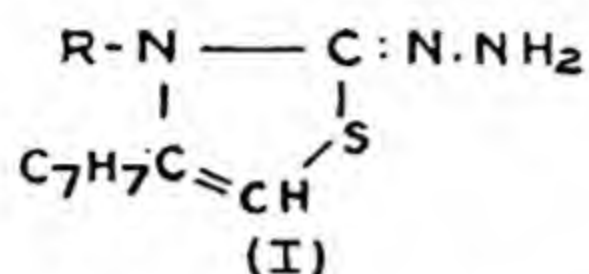
Boiling with pyridine also causes ring-closure of the hydrazo-compounds to yield the same thiodiazoles.



## 39. Thiodiazines. Part VI.

BIRENDRA KUMAR NANDI *and* PRAFULLA KUMAR BOSE,  
Calcutta.

The condensation of p-methyl- $\omega$ -bromoacetophenone with thiosemicarbazides, R. NH. CS. NH. NH<sub>2</sub> (R=H, Alkyl or Aryl) was expected to yield both I and II (cf. Bose, J. Indian Chem. Soc., 1924, 1,50).

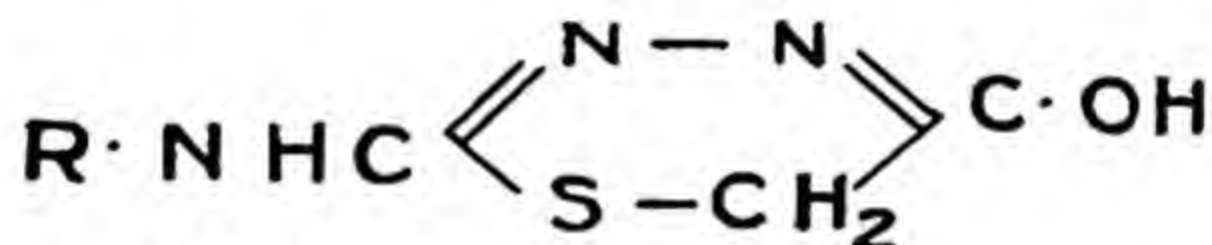


In fact it was found that when R=H, the product has the constitution I. If, however, R is an alkyl or aryl group, the products are found to have the structure II. These results indirectly point out that the ketonic group of p-methyl- $\omega$ -bromoacetophenone is comparatively less active towards the -NH. NH<sub>2</sub> group of thiosemicarbazide than the bromine atom towards the potential thiol group (cf. Guha and Roy-Chowdhury, J. Indian Chem. Soc., 1928, 5, 153).

## 40. Thiodiazines. Part VII.

BIRENDRA KUMAR NANDI *and* PRAFULLA KUMAR BOSE,  
Calcutta.

Chloracetic acid or its ester readily condenses with thiosemicarbazide and 4-substituted thiosemicarbazides forming compounds which, from a consideration of their properties, appear to possess the structure.

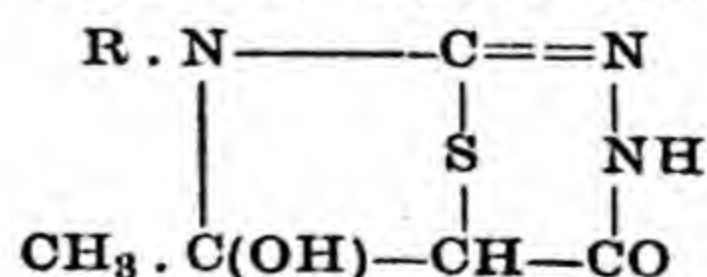


They form monoacetyl and methyl derivatives in the usual way. Thiazoles are not formed in the above condensation even as by-product.

## 41. Thiodiazines. Part VIII.

PRAFULLA KUMAR BOSE *and* BIRENDRA KUMAR NANDI,  
Calcutta.

The condensation of  $\alpha$ -chloroacetoacetic ester and 4-substituted thiosemicarbazides leads to the formation of compounds having the general formula, R.C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>N<sub>3</sub>S. They do not contain the :N.NH<sub>2</sub> or CO<sub>2</sub>Et groups. Moreover, they do not condense with reagents for ketones or give colouration with ferric chloride. These considerations have led the authors to suggest the following formula.



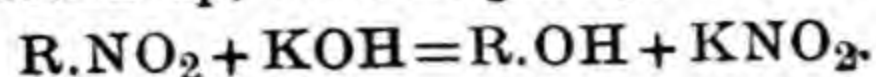
The products are well-defined crystalline substances and are soluble in alkali or acids but not in carbonate solution.



## 42. A qualitative test for nitro-groups in organic compounds.

PRAFULLA KUMAR BOSE, Calcutta.

Aliphatic mono-nitro compounds and poly-nitro-derivatives of benzene, when heated for a short time with concentrated potassium hydroxide solution, break up, at least partly, according to the equation,

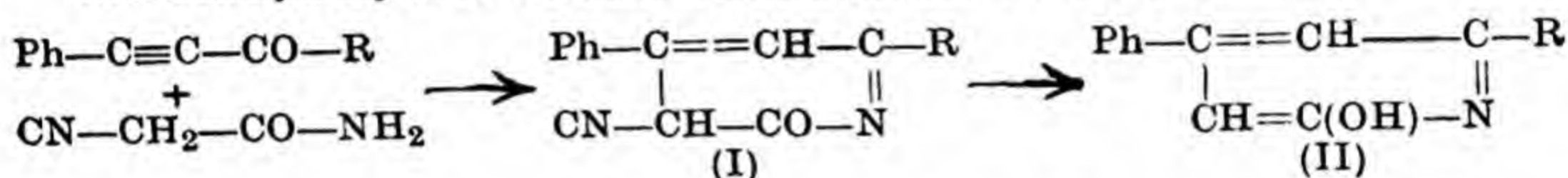


The products after acidification give tests for nitrous acid. Since very delicate tests for nitrous acid are available, the above constitutes a very handy method for the detection of the  $NO_2$ -group in the laboratory. The mono-nitro-derivatives of benzene so far investigated gave negative results.

## 43. Condensation of acetylenic ketones with cyanoacetamide.

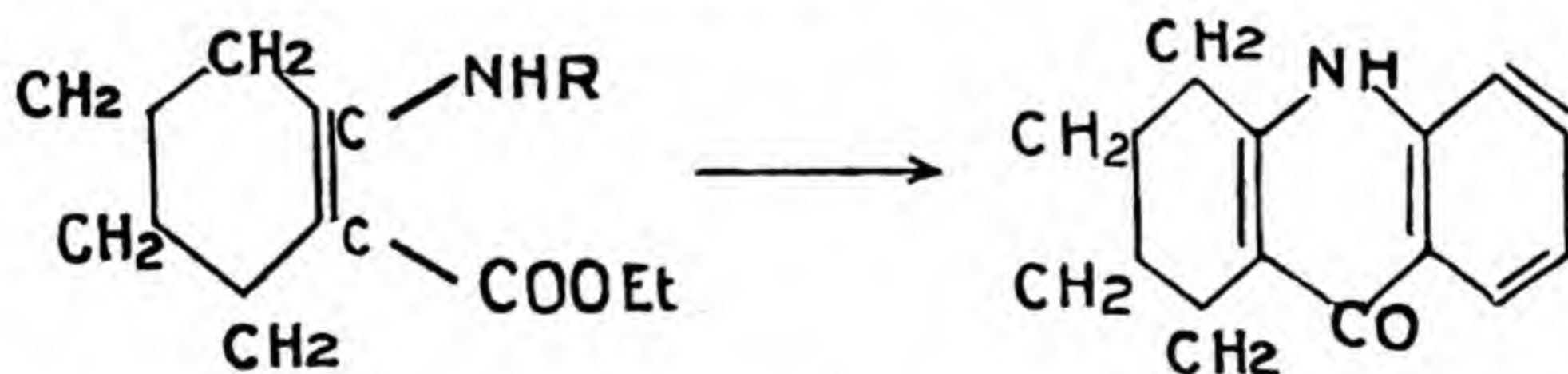
CHITTARANJAN BARAT, Calcutta.

Acetylenic ketones have been condensed with cyanoacetamide in the presence of sodium ethoxide, to form cyano-pyridone derivatives (I), which on hydrolysis gave rise to substituted hydroxy-pyridines (II), identical with compounds obtained by similarly condensing cyanoacetamide and malonamide with arylidene ketones, followed by dehydrogenation and hydrolysis of the condensation products thereby obtained.

44. Formation of heterocyclic compounds. Part V.—  
Synthesis of some tetrahydroacridones.

H. K. SEN and UMAPROSANNA BOSE, Calcutta.

The present work deals mainly with the interaction of ethyl cyclohexanone-2-carboxylate with certain aromatic primary amines at the ordinary temperature. It was already shown (J. Indian Chem. Soc. 1929, 6, 309) by us that at higher temperatures anilides are formed which could be subsequently converted into tetrahydrophenanthridones in the presence of concentrated sulphuric acid. Working at ordinary temperature, anils are formed which on being heated up to boiling temperature, gave tetrahydroacridones.

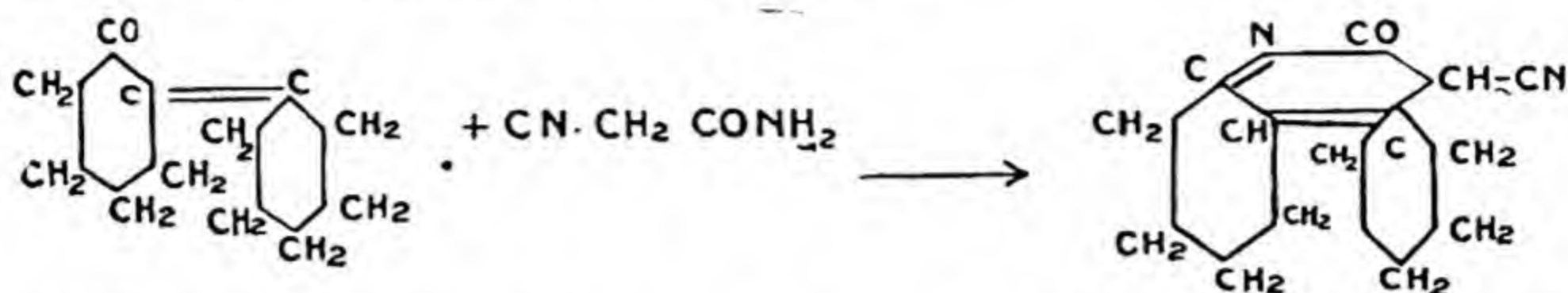
45. Formation of heterocyclic compounds. Part VI.—  
Condensation of cyclohexylidene cyclohexanones with cyanacetamide.

H. K. SEN and NIRMAL KUMAR NEOGI, Calcutta.

The condensations have been carried out in the presence of sodium ethoxide in molecular proportions in absolute alcoholic medium,



the sodium salt of the condensation product being decomposed by passing a current of carbon dioxide. *Cyclohexylidene cyclohexanones* yielded the following type of compounds :—

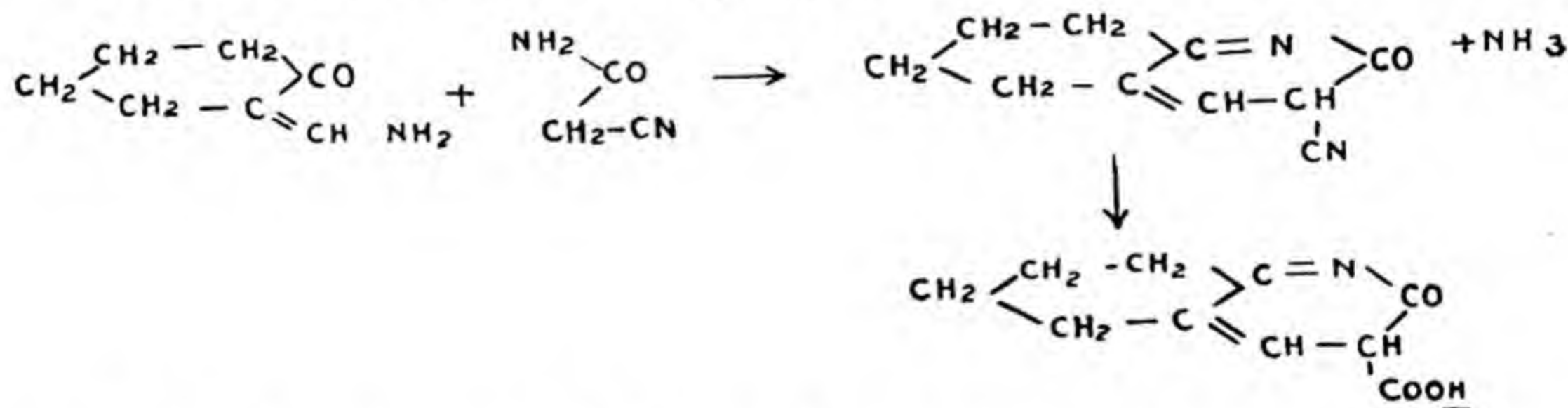


Hydroxymethylene ketones of the *cyclohexylidenes* were also prepared and condensed with cyanacetamide and their difference with the above class of compounds investigated.

#### 46. Formation of heterocyclic compounds. Part VII.— Behaviour of conjugated double bonded systems with cyanacetamide.

H. K. SEN and KANAILAL MANDAL, Calcutta.

In order to exclude the directive influence of sodium ethoxide or Knoevenagel reagents, the condensation of the amide of hydroxymethylene *cyclohexanone* with cyanacetamide was conducted by simply heating the two in molecular proportions at 140°C. The identity of this product m.p. 310° with the condensation product obtained previously from hydroxymethylene *cyclohexanone* and cyanacetamide in the presence of catalysts was established by hydrolysis.



Similar condensation product has been obtained from the amide of hydroxymethylene camphor and cyanacetamide.

When the amide of hydroxymethylene *cyclohexanone* is treated with a slightly alkaline solution of hydroxylamine, the oxime of cyanocyclohexanone is formed which is indicative of the position of the amido group in the hydroxymethylene *cycloketone*. The study of the absorption spectra of the amide and the anilides of the hydroxymethylene *cycloketones* also throws light on the reactivity of the conjugated double bond.

#### 47. Studies in Sulphur Containing Dyestuffs. Part II.— Substituted phenylthioxanthenes and their deriva- tives.

M. V. BETRABET and G. C. CHAKRAVARTI, Bangalore.

Condensation of hydroxybenzhydrols with aromatic mercaptans in the presence of zinc chloride gave highly insoluble red substances with zinc in the molecules. The same condensations when carried out in the presence of freshly prepared zinc chloride with dry HCl gas in occlusion yielded the same type of compounds in greater yields. A



constitution and the course of reaction has now been proposed for them. The elimination of zinc from the compounds yielded the corresponding thioderivatives. In these condensations some alkali insoluble products were isolated which on hydrolysis with alcoholic potash yielded hydroxy phenylthioxanthenes.

The yields of these being not satisfactory other methods of preparation were tried, and finally similar phenylthioxanthenes were obtained by condensing substituted diphenylsulphides with aromatic and substituted aromatic aldehydes.

#### 48. Colour of Complex diazoles. Part V.—Constitution of Thiele's supposed *o*-Benzylene—1:3—benziminazole.

M. V. BETRABET and G. C. CHAKRAVARTI, Bangalore.

Condensation of phthalaldehyde with *orthophenylene* diamine should lead to the formation of benzylyl-*o*-phenylene diamine (I). But Thiele and Falk (*Annalen* 1906, 347, 112) considered the product of this reaction to be *o*-benzylene—1:3—benziminazole (II). In an attempt to prepare compound (II) by condensing phthalide with *o*-phenylenediamine the following products were obtained: (1) Benziminazole-2-benzyl*ortho*-phenylene diamine (III), (2) *o*-aminophenyl-*o*-aminophenyl aminomethyl benzamide and (3) *o*-aminophenyl-*o*-oxymethyl benzamide (IV). Condensation between *o* methoxy benzoic acid and *o*-phenylene diamine gave compounds (III), (IV) and *o*-aminophenyl-ammonium-*o*-oxymethylbenzoate.

On dehydration compound (IV) changed into a product which crystallises in colourless rosettes, m.p. 185°. The synthesis itself establishes the constitution of the product as *o*-benzylene—1:3—benziminazole (II). Thiele and Falk's compound, (m.p. 213.5°C and not 210°C as mentioned by them) must therefore be an isomeric one and identical with benzylyl-*o*-phenylene diamine (I).

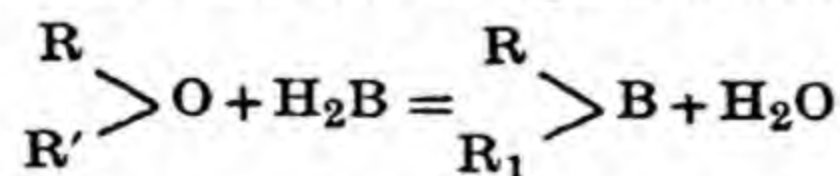
Similar condensation between phthalide and ethylene diamine gave *orthobenzylene*-dihydroiminazole which on oxidation was converted into *orthobenzoylene*dihydroiminazole.

Other condensations between ethylenediamine and phthalic and naphthalic anhydrides, and also between maleic anhydride and *o*-phenylenediamine have been carried out.

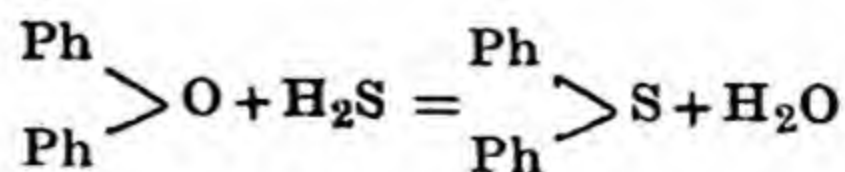
#### 49. Studies in catalytic dehydration.

M. GOSWAMI and MANINDRA NATH SANYAL, Calcutta.

Catalytic dehydration over thoria, in which ethers like diphenyl oxide, anisol, amyl, butyl, propyl, and ethyl ethers take part when ammonia, aniline or sulphuretted hydrogen is passed with them has been studied. It was expected that the general reaction



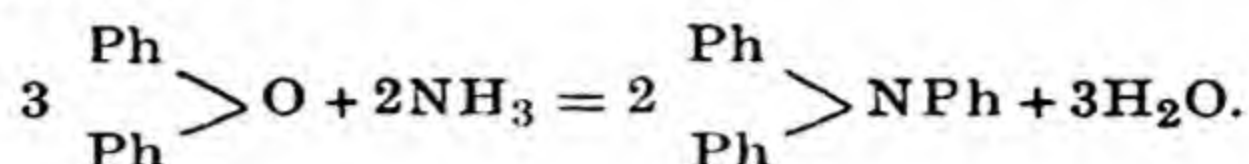
where R and R' are radicals and B stands for S, NH and NPh would take place. It appears that with diphenyl oxide and sulphuretted hydrogen the reaction,



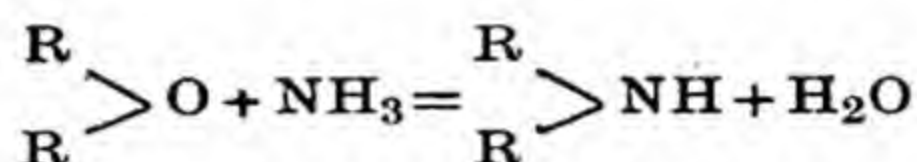
is normal but when the acid hydride is replaced by NH<sub>3</sub> and PhNH<sub>2</sub> abnormal behaviour occurs; the general reaction is extremely sluggish



and only there is slight formation of tertiary amine due perhaps to the following reaction :—



but there is abundant formation of fine crystalline needles in the receiver. These crystals after being filtered and washed with absolute alcohol were examined when it was found that they soften near  $85^\circ$  with evolution of ammonia and leave a residue of thorium oxide when heated on a nickel spatula. The products are still under investigation. Similar types of compounds have been obtained with anisol, but with ethyl, propyl, butyl and amyl ethers there is no such formation and on the other hand appreciable amounts of secondary amine according to equation



are formed.

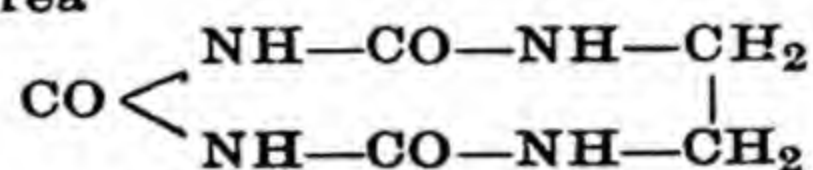
We propose to examine whether such differences in the reaction are attributable to the basic character of oxygen as modified by the attached radicals positive or negative.

#### 50. On Uric Acid.

M. N. RAMASWAMY and P. C. GUHA, Bangalore.

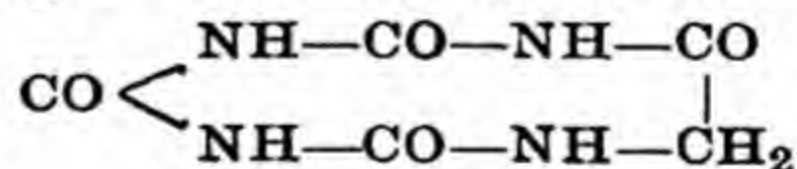
The present paper is a continuation of previous work (Proc. Ind. Sc. Congress, 1929).

Carbo-ethylenediurea



has been obtained as one of the products of interaction between ethylene diamine and carbo-diurethane. On dehydrating this with boiling strong hydrochloric acid, a compound is obtained which shows the characteristic properties of purines, and appears to be desoxyuric acid.

The carbonyl analogue of carbo-ethylene-diurea, namely



has been built up by a series of reactions starting from glycine ester hydrochloride. Attempts are being made to dehydrate this compound. Such dehydration it is expected would result in the formation of uric acid.

#### 51. An Improved Method of preparation of substituted Amides and Hydrazides.

S. M. MISTRY and P. C. GUHA, Bangalore.

Amides like urea, oxamide, malonamide, succinamide, acetamide, etc. react with aromatic amines and hydrazines in presence of boiling *iso*-amyl alcohol to yield the corresponding substituted amides and hydrazides. In most cases crystalline products are obtained in almost quantitative yield which do not require further purification. Aromatic amides, *o*-nitro-substituted aromatic amines and hydrazines do not react. This generalisation is based on the results gathered from about 50 such reactions.



## 52. Researches on the preparation of Aromatic Distibinic Acids.

S. M. MISTRY and P. C. GUHA, Bangalore.

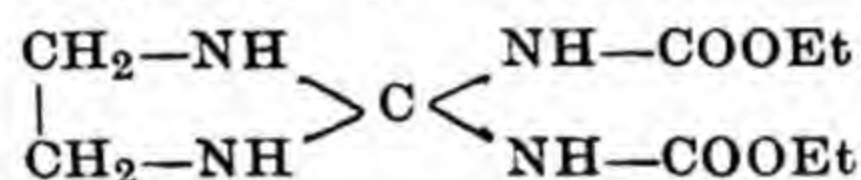
Sym-diaminodiphenyl urea on diazotisation and coupling with antimony trichloride gives a compound which on treatment with alkali is converted into a compound to which the probable formula  $\text{PhNH.CO.NH.C}_6\text{H}_4\text{SbO}_3\text{H}_2$  is suggested. This conclusion has been arrived at from similarity of properties and identical results of analysis of the compound obtained from  $\text{PhNH.CO.C}_6\text{H}_4\text{NH}_2$  by diazotisation, coupling and alkali treatment.

The corresponding compound obtained from benzidin appears to be the anhydride of diphenyl-distibinic acid. *p*-Carbamido-phenyl stibinic acid ( $\text{NH}_2\text{CO.NH.C}_6\text{H}_4\text{SbO}_3\text{H}_2$ ) and *p*-amino-phenyl stibinic acid on being condensed with urea in presence of boiling amyl alcohol give the anhydrides of the compounds whose probable formulæ would be  $\text{CO. (NH.CO.NH.C}_6\text{H}_4\text{SbO}_3\text{H}_2)_2$  and  $\text{CO (NH.C}_6\text{H}_4\text{SbO}_3\text{H}_2)_2$  respectively.

## 53. A derivative of Tetra-aminomethane.

M. N. RAMASWAMY and P. C. GUHA, Bangalore.

When studying the action of ethylene diamine on carbo-diurethane, a compound was obtained, which in the light of the available experimental evidence, is most completely represented by the structure.



## 54. Methyl cyclohexane-2:3-dione-1:4-dicarboxylate.

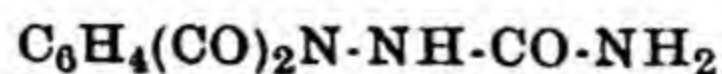
P. P. PATEL and P. C. GUHA, Bangalore.

The preparation was attempted by condensing methyl oxalate with methyl adipate. Contrary to the observations that oxalic ester has no ring-forming action on ethyl adipate or ethyl succinate (Wislicenus and Schwanhauser, Ann. 297, 98), the condensation with adipic ester gives the expected diketone, m.p. 112–113° (mono-semicarbazone, m.p. 170°, violet coloration with ferric chloride), though in a poor yield, together with methyl oxalo-adipate, methyl cyclo-pentanone-2-carboxylate and probably ethyl carbonate. While the work to improve the yield of the diketone by employing varying conditions was in progress a paper by L. Dedusenko appeared in the British Chemical Abstracts (1929, May, 558) wherein a mention of the ethyl analogue of our compound has been made. An alternative method to obtain the same diketone starting from the disodium derivative of  $\alpha\alpha\delta\delta$ -butane-tetracarboxylic ester and oxalyl chloride is also being tried.

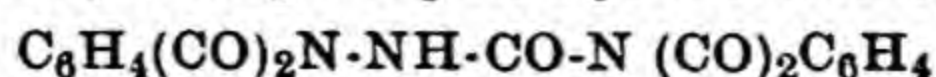
## 55. Condensation of Semicarbazide with Anhydrides of Dibasic Acids.

BANI KANTA BANERJEE, Rajshahi.

When acted upon in molecular proportions, phthalic anhydride produces a monophthalyl derivative of semicarbazide in alcoholic solution,



The monophthalyl derivative again condenses with another molecule of phthalic anhydride yielding a diphtalyl derivative,





In the case of camphoric and diphenic anhydrides, dicamphoryl and didiphenyl semicarbazides only could be obtained. The presence of the free amino group in the monophthalyl compound has been confirmed by condensation with (1) benzaldehyde, salicylaldehyde, and (2) another molecule of phthalic anhydride.

# 56. Heterocyclic derivatives of terpenes and camphors.

HARI DEV, RAM BAHADUR and J. N. RAY, Lahore.

Condensation of hydroxy methylene camphor and menthone with substances like hydrazine gives rise to heterocyclic compounds with bi- and tri-cyclic ring-systems.

# 57. Polynuclear heterocyclic types, derivatives of pentamethine.

G. C. SINGH and J. N. RAY, Lahore.

Condensation of hydrindones with nitro-aldehydes gives nitro-alkylidene hydrindones which on reduction pass to indeno-quinolines. On mild oxidation these are converted into pentamethine derivatives of quinoline.

# 58. On brazilin.

(Late) W. H. PERKIN, R. ROBINSON and J. N. RAY, Lahore.

Catalytic reduction of synthetic hydroxytrimethyl brazilin.

# 59. On the relationship between hydrastine and berberine.

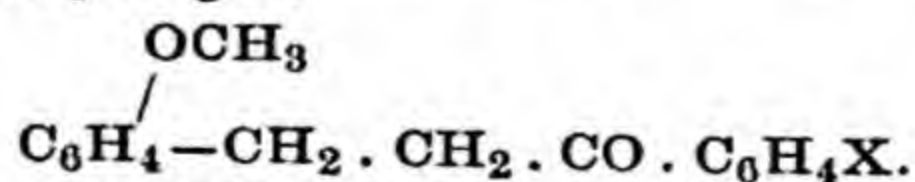
J. N. RAY, Lahore.

Certain intermediate compounds in the synthesis of berberine (Perkin, Ray and Robinson) on methylation and reduction pass into optically inactive hydrastine. The resolution and isolation of optically pure hydrastine is complicated by the fact that an unusually large number of isomers are obtained, the exact stereochemical relation of which is not yet understood. But nevertheless, their synthesis affords a conclusive evidence for the structure of hydrastine and incidentally establishes its relationship with berberine.

# 60. Synthesis in the Catechin Series.

J. N. RAY and STUDENTS, Lahore.

Coumarins on methylation give *o*-methoxycinnamic acids. These on reduction are converted into corresponding hydrocinnamic acids. The esters of these acids condense with phenols and phenolic ethers in presence of 80% H<sub>2</sub>SO<sub>4</sub> to give



These on treatment with HI pass to flavanes which are analogous to cyano-maclurin and catechin in constitution.

# 61. Phthalazines. Part II — Analogues of papaverine.

J. N. RAY and OTHERS, Lahore.

Extension of the work of Aggarwal, Darbari and Ray, (J.C.S. 1929, October) to the phenyl acetic hydrazides leads to the production of bodies analogous to papaverine in structure.



62. *N*-Methylisopelletierine.

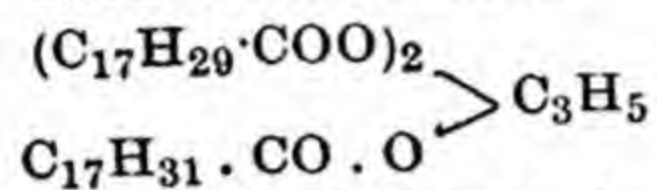
J. N. RAY and STUDENTS, Lahore.

Benzoylpiperidine gives on oxidation benzoylaminovaleric acid, the chloride of which, on treatment with zinc propyl iodide gives the corresponding ketone. The *iso*-nitroso derivative of this undergoes ring closure on hydrolysis forming a substance which is believed to be racemic modification of the above.

## 63. Studies in the isomerism of the higher unsaturated fatty acids and their derivatives.—Part I. Bromination of drying oils.

P. RAMASWAMI AYYAR and V. A. PATWARDHAN, Bangalore.

The oils from the seeds of *Holarrhena antidysenterica* and *Ocimum basilicum* in ethereal or ethyl acetate solution yield on saturation with bromine, in the cold, a crystalline precipitate of a brominated glyceride (m.p. after crystallisation from ethyl acetate 156-157°) which analyses correctly for a dilinolenol-linolin of the structural formula



The bromination of the free acids and their methyl esters is being studied.

## 64. Studies in the synthesis of higher fatty acids by the action of organometallic compounds on derivatives of dibasic acids. Part III.

P. RAMASWAMI AYYAR and V. A. PATWARDHAN, Bangalore.

The action of zinc-propyl-iodide and zinc-*isobutyl*-iodide on 11-bromo-undecylic acid results in the production of a mixture of undecylic and undecylenic acids.

Magnesium methyl iodide gives with methyl azelate 9-methyl-9-hydroxy decylic acid, and the ditertiary glycol (m.p. 67° C).

Magnesium heptyl iodide reacts with succinic anhydride to give 4-ketoundecylic acid (m.p.=80°-80.5° C; semicarbazone, 132°-133° C), along with formation of a hydrocarbon, C<sub>14</sub>H<sub>30</sub>.

## 65. On some derivatives of 4-phenylcoumarin. Part II.

P. C. MITTER and P. K. PAUL, Calcutta.

7-Methoxy-4-phenylcoumarin (Proc. Ind. Sc. Congress. 1929) gives on reduction with sodium and alcohol, 2-oxy-4-methoxy-ββ diphenyl propyl alcohol (m.p. 77°-78°). On heating an alcoholic solution of the substance saturated with hydrochloric acid at 100° for six hours, in a sealed tube, 7-methoxy-4-phenylchroman (b.p. 203-204° 10 mm.) is obtained.

2: 4: 3': 4'—Tetramethoxybenzophenone (from veratroyl chloride and resorcin dimethyl ether, in presence of aluminium chloride) is condensed with bromoacetic ester in presence of zinc. On distilling the product under diminished pressure and hydrolysing the distillate, 2: 4: 3': 4'—tetramethoxy-ββ-diphenylacrylic acid (m.p. 157°) is obtained.

On reduction with sodium amalgam, this gives 2: 4: 3': 4'—tetramethoxy-ββ-diphenyl propionic acid (m.p. 121°).

Treatment with glacial acetic acid and acetyl chloride converts the acrylic acid derivative into 7 methoxy 4-(3': 4' dimethoxy) phenylcoumarin (needles from alcohol, m.p. 163°).



An alternative method of preparing the substance is by the condensation of veratroyl acetic ester with resorcin monomethyl ether in presence of sulphuric acid.

7-Hydroxy-4-(3' : 4'-dimethoxy) phenylchroman is obtained by condensing resorcin with veratroyl acetic ester in a similar manner (m.p. 236°). Methylation with dimethyl sulphate and alkali gives 7-methoxy-4-(3' : 4'-dimethoxy) phenylchroman described above.

The work is being continued.

## 66. Synthesis of Dihydroxychrysazin.

S. V. PUNTAMBEKAR, Bangalore.

Hemipinic anhydride was condensed with *o*-chlorophenol in the presence of anhydrous aluminium chloride. The ring closure of the resulting benzoyl-benzoic acid (m.p. 253°) was achieved by concentrated sulphuric acid at 140°. The product, presumably 1 : 2-dimethoxy-7-chloro-8-hydroxy-anthraquinone, showed the characteristic tests of an hydroxy-anthraquinone. Replacement of the chloro- and the methoxy-groups by hydroxyl groups yielded an anthraquinone, presumably the dihydroxy-chrysazin. It crystallised from alcohol in long dark-red needles (m.p. 323°) and gave purple and red solutions with sodium hydroxide and concentrated sulphuric acid respectively.

## 67. Studies in the anthraquinone series : On 1-oxy-6-methyl- and 2-oxy-6-methylanthraquinones.

P. C. MITTER and ASOKE KUMAR SIRCAR, Calcutta.

3-Nitrophthalic anhydride condenses with toluene in presence of aluminium chloride giving 3-nitro-2-*p*-toluoyl benzoic acid which gives 3-amino-2-*p*-toluoylbenzoic acid on reduction. This on diazotisation gives 3-oxy-2-*p*-toluoyl benzoic acid from which by the action of sulphuric acid 1-oxy-6-methylanthraquinone is obtained.

Similarly, starting from 4-nitrophthalic anhydride and toluene, 2-oxy-6-methylanthraquinone is obtained. This on alkali fusion gives 1 : 2-dioxy-6-methylanthraquinone, and on methylation 2-methoxy-6-methylanthraquinone. On nitration, this latter gives a dinitro-derivative.

## 68. Nitration of 2-oxy-3-methylanthraquinone.

P. C. MITTER and SUDHIR CHANDRA PAL, Calcutta.

Nitration of 2-oxy-3-methylanthraquinone according to the method of Eder and Manoukian (Helv. Chim. A. 1926, 9, 54) gives 1-nitro-2-oxy-3-methylanthraquinone from which on methylation 1-nitro-2-methoxy-3-methylanthraquinone is obtained. On treating with potassium methoxide this substance is converted into 3-methyl alizarin dimethyl ether, which may be de-methylated to 3-methyl alizarin. This latter gives on oxidation 3-methylpurpurin which on reduction with stannous chloride in alkaline solution gives rubiadin.

## 69. Munjisthin. Part II.

P. C. MITTER and HARAGOPAL BISWAS, Calcutta.

Although there are numerous indications pointing to munjisthin being 2 : 4-dioxy-3-carboxyanthraquinone its formation by direct oxidation of rubiadin is rendered difficult by the presence of the two -OH groups in *o*-position to the methyl group. An indirect method of oxidation is therefore being attempted.

2 : 6-Dinitrotoluene is reduced with ammonium sulphide to 2-nitro-6-aminotoluene which is converted into 2-nitro-6-oxytoluene over the diazo

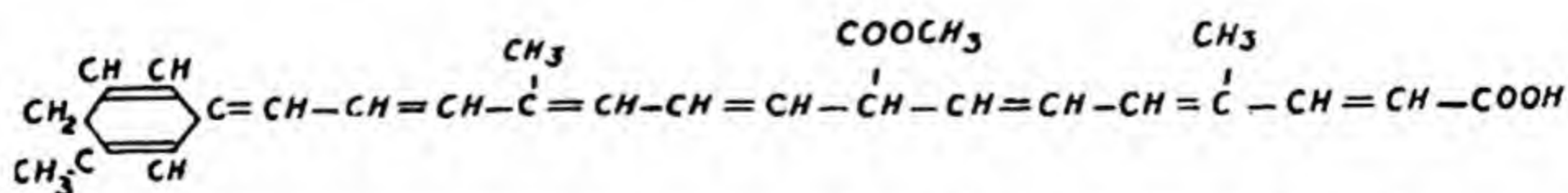


70. The Constitution of "Alkanin" the red colouring matter from Alkanet. Part I.

Liebermann and Romer (Ber. 1887, 20, 2428) mention to have obtained anthracene and methyl anthracene by zinc dust distillation.

K. VENKATARAMAN.

The purely aliphatic structure suggested for bixin by Kuhn and Winterstein and the fulvene structure suggested by Faltis and Viebock are criticised. The deep colour of bixin, the formation of *m*-ethyl toluene by zinc dust distillation, the production of one molecule of *m*-xylene from one molecule of bixin and the necessity for the wandering of a double bond in the explanation of the existence of bixin, *isobixin* and  $\beta$ -*bixin* are facts difficult to account for on the basis of Kuhn's structure. The following structure is in agreement with all the known evidence:—



The quinone structure and the conjugated ethylenic linkages account for the colour, and the production of one molecule of *m*-xylene by reduction; the ozonisation results of van Hasselt and the isomerism of bixin,  $\beta$ -bixin and isobixin are all explicable. While bixin cannot be esterified in the usual way, methyl bixin may be obtained by the action of diazo-



methane (Herzig and Faltis); partial hydrolysis of methyl bixin leads to isobixin and not to bixin. The carboxyl and carbomethoxyl are thus unsymmetrically attached in the bixin molecule.

## 72. Alkaloids of *Hedyotis Auricularia*, Linn.

BIMAN BIHARI DEY, Madras.

A general examination of this plant showed that it contained considerable amount of tannin, some reducing sugars and glucosides with one or more accompanying enzymes which caused fermentation with evolution of  $\text{CO}_2$ , a small quantity of a fixed oil, a fruity-smelling ester, and a basic principle precipitated by the common alkaloidal reagents. The latter is found to occur in all parts of the plant, the roots containing the largest amounts. An assay of the alkaloids (a) in the leaves and stems, and (b) in the roots, showed that the former contained 0.1%, and the latter 0.3% approximately. The air-dried, powdered roots which were selected for detailed examination, gave to petroleum ether (b.p.  $60^\circ\text{--}70^\circ$ ) 1.1%, ether 2.6%, alcohol 8.9%, and water 7.7% extracts respectively. The alcoholic extract was found to contain the whole of the alkaloids.

The alkaloids were purified through their mercuri-chlorides. A sparingly soluble hydrochloride separating from methyl alcohol and ether in nearly colourless, hard prismatic crystals, sintering at  $235^\circ\text{C}$ , and melting with decomposition at  $258^\circ\text{C}$ , and a soluble hydrochloride which did not crystallise, but remained as a pale yellow thick syrup, have been isolated. As a mean of three closely agreeing estimations, the chlorine in the former was found to be 10.3%; assuming the salt to contain only 1 molecule of  $\text{HCl}$ , the molecular weight of the alkaloid hydrochloride should approximate to 343. The hydrochlorides dissolved in water as well as alcohol, with a bright bluish-green fluorescence.

Both the sparingly soluble, and the soluble hydrochlorides, on treatment with cold dilute caustic alkalis, precipitated the alkaloid or alkaloids as a fine golden yellow powder. The latter looked pure, and remained unchanged when kept under water for weeks. On filtering and attempting to dry it, however, it rapidly changed to a dark brown sticky mass from which the original hydrochlorides could not be reproduced. The change appears to be one of oxidation, and the reaction is being studied more closely.

The picrate corresponding to the alkaloid of the sparingly soluble hydrochloride, separated in well-formed, deep yellow crystals of a pyramidal structure, melting with effervescence at  $264^\circ\text{C}$  ( $\text{N} = 15.9\%$ ).

## 73. Constitution of the active principle of *Corchorus Capsularis*.

NIRMAL KUMAR SEN, Dacca.

Corchorin, the active principle of jute-seeds has been obtained in colourless prisms, melting and decomposing at  $174\text{--}175^\circ\text{C}$ . It is a glucoside having an extremely bitter taste and has saponin-like properties but unlike saponin it has no hemolytic action on red blood corpuscles. It is dextrorotatory  $[\alpha]_D = 33.4$  and has the molecular formula  $\text{C}_{22}\text{H}_{36}\text{O}_8$  [mol. wt. = 423, 427 in glacial acetic acid and 435 and 439 in phenol (Raoult)]. It gives an acetyl derivative m.p.  $83\text{--}85^\circ\text{C}$ , and with bromine yields the crystalline monobromo-corchorin-dibromide, m.p.  $100^\circ\text{C}$ . On hydrolysis by mineral acids it yields glucose and a yellow product having the composition  $\text{C}_{16}\text{H}_{26}\text{O}_3$  which forms rhombic plates melting and decomposing at  $114\text{--}115^\circ\text{C}$  and it has been termed "corchogenin." Corchogenin contains a double bond since it readily gives a crystalline dibromoderivative and contains no methoxy group. It reduces ammoniacal silver nitrate in alcoholic solution and on prolonged heating with phenyl-



hydrazine gives an amorphous hydrazone. It yields a trichloro-derivative ( $C_{16}H_{23}Cl_3$ ) when heated with  $PCl_5$ , m.p.  $124-125^\circ C$ . On oxidation with potassium permanganate, corchorin yields a crystalline acid, m.p.  $57-60^\circ C$ , having a mean molecular weight 456.5, which on hydrolysis yields an acid and glucose.

74. Morellin—a Yellow Crystalline Colouring Matter in the Pericarp of the Seeds of *Garcinia Morella*, Desr.

B. SANJIVA RAO, Bangalore.

The colouring matter  $C_{30}H_{34}O_8$  is obtained in a yield of 1.6 per cent. by extraction of the seeds with methyl alcohol and melted at  $153-154^\circ$ . During its investigation, the following derivatives have been prepared and described: acetyl derivatives ( $C_{38}H_{42}O_{10}$ , m.p.  $178-179^\circ$ ), bromoderivative ( $C_{30}H_{34}O_8Br_4$ , m.p.  $138-139^\circ$ ) oxime ( $C_{30}H_{36}O_8N_2$  m.p.  $148-149^\circ$ ) phenylhydrazone, (m.p.  $258^\circ$ ), *p* nitro-phenylhydrazone (m.p.  $201-202^\circ$ ) and the methoxy derivative (m.p.  $101-102^\circ$ ).

75. Chemical examination of Fenugreek (*Trigonellum foenum Graecum*).

M. SREENIVASAYA and B. N. SASTRI, Bangalore.

Ether extracts a semidrying oil with the characteristic pungent odour. Seventy per cent. alcohol extracts phospholipins which get precipitated by an alcoholic solution of cadmium chloride. On addition of acetone a white amorphous body separates which is hygroscopic, optically active (dextro), contains nitrogen and phosphorus in stoichiometric ratio of 3:1 and on acid hydrolysis liberates a reducing sugar. Further work is in progress.

76. Chemical examination of the roots of *Bragantia Wallichii* (Br.).

B. L. MANJUNATH and D. V. VENKATASUBBAIYA, Bangalore.

*Bragantia Wallichii* belongs to the family of *Aristolochiaceae*, (Sams. *Chakrani*). The root in the form of a paste is used in medicine. The material for the following work was collected in Shimoga district (Mysore state).

Successive extraction with the following solvents.	Per cent. of extract.
Petroleum ether (b.p. $40-50^\circ$ )	.. 0.5
Ethyl ether .. ..	.. 2.2 (fluorescent solution)
Chloroform .. ..	.. 0.6 ( " " )
Ethyl acetate .. ..	.. 0.6
Alcohol .. ..	.. 4.4
Total	.. 9.3

The occurrence of an alkaloid has been established. The constituents (volatile in steam) amounted to 0.01 %. An aqueous extract of the roots gave tests for starch and reducing sugars. No tannin material could be detected.

The paper deals with the chemical and pharmacological study of the various constituents.



77. Chemical examination of the seeds of *Cassia Tora* (Linn.).

H. S. JOIS and B. L. MANJUNATH, Bangalore.

The occurrence of the glucoside of a substance of the nature of emodin in the seeds of *Cassia tora* has been recorded in the literature. The following work is a more detailed study of the various constituents of the seeds.

Successive extraction with the following solvents.				Per cent. of extract.
Petroleum ether (b.p. 40–50°)	..	..	..	5.2
Ethyl ether	..	..	..	1.2
Chloroform	..	..	..	1.6
Ethyl acetate	..	..	..	2.2
Alcohol	..	..	..	6.2
Total				16.4

Constituents volatile with steam = 0.003% (pale yellow crystals).

The petroleum ether extract gave a pale brown oil which had the following constants:—

Sp. gravity at 25°/25°	..	..	0.8969
Refractive index at 25°	..	..	1.4743
Saponification value	..	..	154.2
Iodine value (Hanus)	..	..	90.7

A more detailed study of the oil particularly because of its medicinal value in skin diseases, will form the subject of another communication.

Ethyl ether extracted a small amount of the colouring matter occurring in the free state. The glucoside was obtained mainly in the ethyl acetate and alcohol extracts. The seeds did not contain any alkaloids. The presence of an enzyme has been established. An aqueous extract gave tests for reducing sugars as well as for hydrolysable polysaccharides. Starch and tannin were absent.

78. Chemical examination of the seeds of *Psoralea Corylifolia* (Linn.).

B. L. MANJUNATH, Bangalore.

The seeds of *Psoralea corylifolia* (*Bhavancha* in Samskrit) are used in Ayurvedic medicine. The present investigation forms a systematic analysis of the various substances present in the seeds.

Successive extraction with the following solvents.				Per cent. of extract.
Petroleum ether (b.p. 40–50°)	..	..	..	8.0
Ethyl ether	..	..	..	10.8
Chloroform	..	..	..	3.7
Ethyl acetate	..	..	..	3.2
Alcohol	..	..	..	8.2
Total				33.9

The percentage of the essential oil was found to vary.

The petroleum ether extract gave a dark brown viscous oil which had the following constants:



Sp. gravity at 25°/25°	..	..	0.9689
Refractive index at 25°	..	..	1.5137
Saponification value	..	..	133.2
Iodine value (Hanus)	..	..	113.3

The oil is being investigated further.

The ether extract contained the entire colouring matter. The seeds did not contain any alkaloidal constituents. An aqueous extract gave tests for the presence of a small amount of reducing sugars, and for a considerable amount of hydrolysable polysaccharides. Starch and tannin were absent.

79. Proximate Analysis of *Coscinium Fenestratum*, Coleb.  
M. C. TUMMIN KATTI and (the late) V. P. SHINTRE,  
Bangalore.

The alcoholic extract of the stems of the plant has been found to contain the following compounds.

Palmitic acid, a hydrocarbon (m.p. 68-69°), phytosterolin (sitosterol-glucoside), sitosterol (m.p. 135-136°), ceryl alcohol (m.p. 78-79°), saponin, glucose and a considerable amount of a mixture of alkaloids.

80. Chemical Examination of the Bark of *Terminalia Arjun*.  
A. JANAKI RAM and P. C. GUHA, Bangalore.

The present work describes the isolation of two organic acids and a phytosterol in addition to confirming the presence of tannins and colouring matters.

81. Cantharidin from *Zonabris (Mylabris) Pustulata*,  
(Indian).

B. H. IYER and P. C. GUHA, Bangalore.

*Zonabris (Mylabris) pustulata*, commonly known as blister-beetles were collected locally and examined for the cantharidin content. A method of extraction has been found out which given an yield of 2.1-2.3% of cantharidin. About 0.5 to 0.6 % is found to exist in the salt-form, the remainder being present as free cantharidin. The dried insects yield 12 to 12.5% fat.

Synthesis of deoxycantharidin is being effected starting from *o*-methylcyclohexanone. After obtaining 1:2-dibromo-1:2-dimethylcyclohexane, its dinitrile is prepared. It is expected that the dinitrile will give the dicarboxylic acid and the corresponding anhydride, the latter of which will be deoxycantharidin.

82. Oil from cantharides insects.

B. H. IYER and P. RAMASWAMI AYYAR, Bangalore.

This oil obtained as a by-product in the isolation of cantharidin from the insects had a sp. gr. 30°/24° of 0.910, after neutralisation and removal of admixed cantharidin.

The crude fatty acids have an I.V. of 42.6, and an equivalent weight of 220. When analysed by the lead-salt-alcohol method they gave 31 per cent. of saturated acids and 69 per cent. of unsaturated acids. The former have an equivalent weight of 260 and the latter seems to be a mixture of oleic and a small quantity of cantharidic acids.



83. Oil from the seeds of *Ocimum Basilicum* (Linn).

P. RAMASWAMI AYYAR and V. A. PATWARDHAN, Bangalore.

The seeds yield to petroleum ether 9.5 per cent. of oil, which has been characterised by the following properties:

Sp. gr. at 25°C	=0.933
Ref. index at 25°C	=1.48
Iod. value	=166.6
Sap. value	=191.8
Acetyl value	=16.5
Unsaponifiable matter	=1.2

The fatty acids have been resolved by Twitchell's method into saturated (7.4 per cent.) and unsaturated (92.6 per cent.) acids. The former consists mostly of palmitic acid mixed with a small quantity of stearic acid.

The latter are composed of two isomeric linolenic acids, linolic acid and oleic acid.

The sterol obtained from the unsaponifiable matter melts at 115-120°C.

84. Oil from the seeds of *Schleichera Trijuga*, Willd.

P. RAMASWAMI AYYAR and S. M. PATEL, Bangalore.

A genuine specimen of the expressed oil obtained from Palghat had the following physical and chemical characteristics:

Sp. gr. at 15°C	=0.918
Ref. index at 25°C	=1.466
Sap. value	=223.0
Iod. value	=52.8
Unsaponifiable matter	=3.7

The fatty acids were resolved by the lead-salt-alcohol method into saturated (43 per cent.) and unsaturated (57 per cent.) acids. The former are composed mostly of palmitic (18 per cent.) and *n*-eicosanic acids (82 per cent.) The latter consists mainly of oleic acid.

From the unsaponifiable matter pure sitosterol has been isolated.

85. Oil from the seeds of *Amoora Rohituka*.

P. RAMASWAMI AYYAR and V. A. PATWARDHAN, Bangalore.

The kernels (78% of the seeds) yield to petroleum ether 45% of a fixed oil, and the cake yields to alcohol about 1% of a solid resin. The oil has the following properties:

Sp. gr. at 15°C	=0.931
Ref. index at 25°C	=1.480
Saponification value	=186.0
Iod. value	=130.0

The oil does not yield a crystalline bromoglyceride on bromination and resembles poppy seed oil in this respect.

86. The constituents of the Essential Oil from the leaves of *Cinnamomum Zeylanicum*, Breyn: The occurrence of  $\gamma$ -terpineol.

(The late) V. P. SHINTRE and B. SANJIVA RAO, Bangalore.

The leaves obtained from the Western ghats yielded 0.2 per cent. of an oil. The authors have isolated the following:—*l*- $\alpha$ -pinene,  $\beta$ -phellandrene



(3.5 per cent.) eugenol (15 per cent.) terpene alcohols mainly  $\gamma$ -terpineol (2.1 per cent.) sesquiterpenes mainly *l*-cargophyllene (62 per cent.) sesquiterpene alcohols (6.8 per cent.)

87. The Essential Oil from the Flower-heads and stems of  
*Andropogon Kuntzeanus*, Hack, *Forma Foveolata*,  
Hack.

B. SANJIVA RAO, Bangalore.

The oil was obtained in a yield of 0.27 per cent. and consisted of terpenes (30 per cent.) *l*- $\alpha$ -pinene, *l*-camphene, *l*-limonene, *l*-borneol, sesquiterpenes (4 per cent.) sesquiterpene alcohols (61 per cent.)

88. Examination of unsaturated acids in fish oil.

J. K. CHAUDHURY and P. B. SARKAR, Dacca.

The stomach oil of "*Labeo rohita*"—an Indian fresh-water fish commonly known in Bengal as 'Rohit'—was found to consist of 28.1% saturated acids (I.V. 2.4) and 71.9% of unsaturated acids (I.V. 180.8). The unsaturated acids were (1) oxidised with very dilute potas. permanganate at 0°, and (2) brominated at -10° in dry ethereal solution. The oxidation method revealed the presence of *asellinic* and *oleic acids* while the bromination method confirmed the following acids which were also quantitatively determined:—*Tetrosapentenoic acid*, *Linolenic acid*, and *Hexadecatrienoic acid*.

Hexadecatrienoic acid (having 16 atoms of carbon and 3 double bonds) whose presence in fish oil was suspected by Brown and Beal, has been isolated (as hexabromide) and examined by the authors for the first time while tetrosapentenoic acid has not been found in any fish oil before. The only experimental evidence of the existence of this latter acid is found in the work of Carter (J.S.C.I. 1928 47, 31T,) who found it in mutton bird oil. The bromo-derivative of Carter however blackened at a much lower temperature (200°) than ours (242°).

It may be noted that the separation of the polybromides could not be effected by the usual method but only with the help of chloroform which has been found very suitable for the purpose. The detection of *asellinic acid* having an odd number of carbon atoms, whose existence has been doubted by several investigators, confirms the work of Fahrion (Chem. Umsch. 1927 24, 6.).

89. Chemical and Physico-chemical Examination of *Eupatorium Ayapan* and *Justicia Gandharussa*.

N C. NAG and K. BOSE, Calcutta.

The two plants are important medicinal plants with distinctive physiological actions, which are likely to be associated with certain definite chemical constituents. The plants have been grown at the Bose Institute at Calcutta and also at Falta, 30 miles down the Ganges. Changes in the amounts of chemical constituents under varying conditions of locality and of seasons have been studied.

Pressed out sap is distinctly acidic, pH value ranging between 6.07 and 5.75 (the higher values are obtained during the rains). Refractive index at 30° for the two varieties examined on the same day was found to lie between 1.3432 and 1.3462.

Of *Justicia Gandharussa* there are two varieties, one purple and the other green twig variety. The purple variety is very rich in chlorine and total nitrogen as also in nitrate content. There is however great variation



with the season changes, chlorides (and to some extent the nitrates) coming to almost half the dry season values.

The pH value of sap from purple variety lay between 7.86 and 7.68 with a tendency towards neutrality during the rains. Refractive index was 1.3425.

Green variety of *Justicia Gandharussa* had low nitrogen content. Green *Justicia Gandharussa* sap was alkaline but the pH value was nearer 7.01, thereby verging on acidity, thus standing intermediate between purple *Gandharussa* and *Eupatorium Ayapan* during the rains.

A quantitative study of the following constituents were made, both in the ash and in the dry matter obtained from the plants:—

Moisture, ash,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ , Cl,  $\text{NO}_3$ , total N,  $\text{SO}_3$ , Fe, CaO, MgO, Na, K, fibre, sugar convertible carbohydrates, etc., (suitable methods had to be devised in some cases).

#### 90. Alkaloids in *Diospyros Cardifolia*.

MOHD. RAFAT HUSAIN SIDDIQI and Q. A. MANSURI, Aligarh.

The dried and powdered fruits were extracted with lime and water. The colouring matters, etc., were removed by means of lead acetate and lead by means of sulphuretted hydrogen. The filtrate was concentrated and tested with the alkaloidal reagents which indicated the presence of alkaloids. Further work is in progress.

#### 91. Preliminary Examination of the Constituents of *Hydrocotyle Asiatica*.

M. A. WALI and TUMMIN KATTI, Bangalore.

Seven crystalline substances were isolated but the quantities were too small to be identified. Presence of reducing sugars and a phytosterol, b.p.  $120^\circ$ — $122^\circ$  was indicated.

#### 92. Investigation of *Aristolochia Indica*.

M. A. WALI, Bangalore.

*Aristolochia Indica* was found to contain an alkaloid.

#### 93. Halogenation. Part IV.—Halogenation of Aromatic Acids.

P. S. VARMA and P. B. PANICKER, Benares.

A good yield of *m*-bromobenzoic acid has been obtained by brominating benzoic acid in presence of a mixture of fuming nitric and nitrosulphonic acids, or sodium nitrite and fuming sulphuric acid. Iodobenzoic acid is also obtained comparatively in good yield in presence of the same reagents. With *p*- and *o*-toluic acids, mono-bromo-, and mono-iodo-derivatives have been obtained. *m*-Toluic acid is not brominated or iodinated under the same conditions. Anisic acid gives bromo- and iodo-derivatives whilst phthalic, isophthalic and terephthalic acids are unaffected. *p*-Nitro, *p*-chloro-, and *p*-bromo-benzoic acids are also not halogenated.

#### 94. Halogenation. Part V.—Halogenation of Naphthalene, $\beta$ -Naphthylamine and $\beta$ -Naphthol.

P. S. VARMA and D. N. MAZUMDAR, Benares.

Attempts have been made to iodinate naphthalene directly under different conditions in presence of a number of substances, such as pyridine,



concentrated nitric acid, fuming nitric acid nitro-sulphonic acid, potassium persulphate, chromic acid, fuming sulphuric acid, a mixture of fuming nitric and sulphuric acid, and iodic acid. Iodonaphthalene has been obtained in most cases.  $\beta$ -Naphthylamine has resisted up till now all attempts of iodination.  $\beta$ -Naphthol is, however, iodinated and an iodo-derivative of it has been obtained in a comparatively good yield in presence of ammonia.

Naphthalene is more easily brominated in presence of nitro-sulphonic and fuming nitric acid mixture.

### 95. Halogenation. Part VI.—Bromination and Iodination of Anthraquinone.

P. S. VARMA and A. SUBRAMANYAM, Benares.

Anthraquinone has been brominated and iodinated in presence of a few foreign substances, and mono-bromo-, dibromo-, mono-iodo-, and di-iodo-anthraquinones have been obtained in fairly good yields.

### 96. Halogenation. Part VII.—Replacement of Sulphonic Groups in Aromatic Amino-sulphonic Acids by Halogens.

P. S. VARMA and G. SANYASAYYA, Benares.

The action of halogens on the sulphonic acid derivatives of mono-methyl-, di-methyl-, mono-ethyl-, and di-ethyl-anilines, diphenylamine, and  $\alpha$ -naphthylamine has been studied. In the case of the first four compounds the sulphonic groups are completely replaced by halogens. No product is obtained from diphenylamine. The sulphonic groups in naphthylamine are not replaced by halogens though halogen derivatives are obtained in most cases.

### 97. Nitration of Anthracene and its Derivatives.

P. S. VARMA and A. SUBRAMANYAM, Benares.

By treating anthracene with nitric acid, anthracene is converted partly into anthraquinone and partly into nitro-anthraquinones. All attempts to nitrate the di-nitro-anthraquinone have proved unsuccessful. Mono-bromo-anthraquinone is converted into bromo-nitro-anthraquinone at lower temperatures but at higher temperatures only nitro-anthraquinone is obtained. It has been possible to get a bromo-di-nitro-anthraquinone also by increasing the quantity of nitric acid. In the case of chloro-anthraquinone only a mono-nitro-derivative has been obtained. Under the same conditions iodo-anthraquinones are decomposed into anthraquinone and iodine.

### 98. The Oxidation of the Paraffin Wax (Preliminary).

P. S. VARMA and H. R. KRISHNAN, Benares.

Attempts have been made to oxidise the paraffin wax by means of atmospheric oxygen in presence of nitric oxide at different temperatures. In the oxidation products at 140–145° (total yield 70%) arachidic, non-decoic, palmitic acids and a C<sub>12</sub>-hydroxy acid have been obtained; at 170–175°C (yield 76%) in addition to the above tridecoic acid and hydroxy tridecoic acid have been obtained. Small quantities of carbon dioxide, acetic acid, butyric acid and nitroethane have also been found among the oxidation products.



99. The Reduction of *o*-Nitrotoluene.

P. S. VARMA and V. ANNA RAO, Benares.

Magnesium powder in presence of methyl or ethyl alcohol and aqueous ammonium chloride solution gives *o*-azoxytoluene (89%). Zinc dust under similar conditions and stannous chloride (in alkaline medium) also yield *o*-azoxytoluene. *o*-Azotoluene is obtained by the action of sodium methoxide or ethoxide at 100°. Aluminium wire (or dust), zinc dust and stannous chloride (alkaline medium) also yield *o*-azotoluene. With aluminium or zinc dust *o*-hydrazo-toluene is also obtained. A good yield of hydrazo-toluene is obtained by the action of ammonium sulphide on *o*-azotoluene. *o*-Toluidine is the main product when sodium sulphide or tin or stannous chloride in hydrochloric acid is used as a reducing agent.

100. NITRATION OF *m*-dichlorobenzene.

H. S. JOIS and B. L. MANJUNATH, Bangalore.

The products of the nitration of *m*-dichlorobenzene are 4: 6-dichloro-1: 3-dinitrobenzene (m.p. 102–103°, yield 80%), 2: 4-dichloro-1: 3-dinitrobenzene (m.p. 70–73°, yield 5%), and 3: 4-dichloro-1: 2-dinitrobenzene (m.p. 50–53°, yield 5%). The formation of the latter would be the result of a rearrangement of the molecule during the process of nitration.

## 101. 2: 4-Dinitrophenylhydrazine as Reagent for Sugars.

VINAYAK NARAYAN PATWARDHAN, Bangalore.

2: 4-Dinitrophenylhydrazine forms the corresponding hydrazones with monosaccharides. Compounds with glucose, mannose and arabinose have been prepared.

## 102. Action of Light on Tyrosinase.

D. NARAYANAMURTI and C. V. RAMASWAMI AYYAR, Bangalore.

Tyrosinase (J. Ind. Inst. Sc., 1929, 12A, 109) is activated by exposure to the rays from a quartz mercury lamp. The effect has been studied with regard to the purity of the preparation, pH etc. The mechanism of activation by the rays has also been investigated both from the physico-chemical and chemical points of view.

## 103. Purification of Tyrosinase.

D. NARAYANAMURTI and C. V. RAMASWAMI AYYAR, Bangalore.

Tyrosinase (prepared from *Dolichos lab lab*) purified by the following methods has been studied: (a) ordinary dialysis, (b) electro-dialysis, (c) ultrafiltration, (d) electro-ultrafiltration, (e) repeated precipitation of the dialysed extracts with alcohol, and (f) adsorption followed by elution. The influence of natural salts on these preparations has also been investigated.

## 104. Proteins of Cumbu.

D. NARAYANAMURTI and C. V. RAMASWAMI AYYAR, Bangalore.

The major portion of the proteins occurring in cumbu (*Pennisetum typhoideum*) is best extracted by 70% alcohol. The protein thus extracted has been purified by repeated precipitation and the nitrogen distribution by Van Slyke's method and estimation of special units by



colorimetric methods carried out. The physical properties of the protein have also been studied.

105. Proteins of *Dolichos Lab Lab*.

D. NARAYANAMURTI and C. V. RAMASWAMI AYYAR, Bangalore.

The kernel contains about 25% protein about 85% of which is extracted by water. To avoid tyrosinase action the extracts have been subjected to electrodialysis in a suitably constructed electrodialyser out of contact with air and the pure product so obtained has been investigated with regard to its nitrogen distribution and physical properties.

106. Influence of Charcoals on the Biological Oxidation of sulphur.

C. V. RAMASWAMI AYYAR, Bangalore.

Charcoals (ordinary as well as ash-free) have been found to exert a marked influence on the biological oxidation of sulphur. The results of experiments conducted to elucidate the mechanism of this activation are discussed.

107. The nature of amylase. Part II.

D. NARAYANAMURTI, Bangalore.

Amylase is considerably increased in activity on electro-ultrafiltration. Further evidence based on ultrafiltration experiments is brought forward in support of the two-enzyme theory of amylase.

108. Chemical study of the Germination of Groundnut.

D. V. KARMARKAR, Bangalore.

Groundnut (*Arachis Hypogea*) contains about 50% oil, 30% protein, 10% sugars and a little starch. On germination, the oil decreased from 46.8 to 25.96% and was accompanied by an increase in starch content from 3.6 to 17.0%. Sugar decreased in the beginning but later there was increase upto 13%. Cotyledons and embryos were also examined separately. Total protein remained unaltered throughout the period of the investigation.

109. Fermentation of Pentoses by *Bacillus Acetoethylicus*.

VINAYAK NARAYAN PATWARDHAN, Bangalore.

The hydrolysed product of straw served as the fermenting medium. Dry straw was extracted with sulphuric acid (6%) by steaming for six hours at atmospheric pressure. The extract was concentrated and the sugar content was brought to 7 or 8%. The bacillus which had been specially trained to ferment high concentrations of sugar was inoculated in the sterile medium. The fermentation was allowed to proceed for 8-10 days and the contents distilled. Sugar from the residue and alcohol and acetone from the distillate were estimated.

About 86% sugar disappears during fermentation. The alcohol and acetone together amount to about 23-25% of the sugar fermented. Favourable conditions leading to a higher yield of the alcohol and acetone mixture are being worked out.



110. Amylase from *Eleusine Coracana*.VINAYAK NARAYAN PATWARDHAN and NUGGEHALLI  
NARAYANA, Bangalore.

The enzyme from the malt was extracted with 20% alcohol and precipitated by 95% alcohol. Examination of the hydrolysing action showed the enzyme to be actively liquifying and saccharifying. The action of the enzyme on potato starch has been studied. The optimum temperature for the enzyme lies between 55° and 60° and optimum reaction is between pH 4.8 and 5.0. The precipitated enzyme as well as the extract loses its activity after long dialysis in collodion bags at a temperature of 3°–4° C. In this behaviour it resembles the amylase from *Zea mais*.

## 111. Asparaginase from maize.

C. V. PARAMASIVAN, Bangalore.

The enzyme was prepared from germinated maize which was ground with quartz sand in a mortar with nearly two to three times its weight of water and filtered through cloth. The liquid was centrifuged and the enzyme precipitated by the addition of a sufficient quantity of ice cold 90% alcohol; separated by centrifuging, washed with ether, dried at 30°, powdered and preserved. The action on asparagine was followed by estimating the amount of ammonia formed from time to time. The effects of reaction, dialysis, inorganic salts and amino-acids on the course of the hydrolysis were studied. The velocity constant calculated according to the monomolecular formula was observed to increase with time.

## 112. Studies on some proteolytic enzymes of vegetable origin. Part I.—Peptidases.

C. V. PARAMASIVAN, Bangalore.

The enzymes from malted cholam and maize were prepared and the conditions relating to their action on some of the simpler dipeptides were studied.

113. Studies in the nutrition of the lac insect. Part VI.  
—A physico-chemical study of the tissue fluids of some host plants.

B. H. KRISHNA and M. SREENIVASAYA, Bangalore.

The hydrogen-ion-concentration, buffer value, osmotic pressure and electrical conductivity of the tissue fluids have been determined at different periods of the insects' life-cycle. Tissue fluids having a reaction range of pH 5–5.5 are found to be more suitable than more alkaline fluids. Higher buffer values characterise the tissue fluids derived from stems attacked by insects.

The mean M.W. of the solutes in the fluids, calculated from the total solids and the osmotic pressure point to the presence of substances of high molecular weight in the tissue fluids of host plants which are reputed to be excellent hosts for lac production.

114. Studies in the nutrition of the lac insect. Part VII.  
—Biochemical changes induced in the host on insect attack.

B. H. KRISHNA and M. SREENIVASAYA, Bangalore.

A sudden increase in the nitrogen and phosphorus contents without a proportionate increase of calcium in the tissue fluids of the stem is



brought about through the attack of the insect. Generally the drain effected by the insect on the host is with regard to nitrogen, phosphate, and carbohydrates. If the heavy demand of nitrogenous and phosphatic materials is met by direct application of suitable manures, the host will yield heavy crops of lac and big swarms of larvæ.

With regard to the carbohydrate supply, however, a predominant accumulation of starch in the stems should be ensured before the infection.

### 115. Studies in the nutrition of the lac insect. Part VIII —Nutrition in relation to parasitism.

B. H. KRISHNA and M. SREENIVASAYA, Bangalore.

The high acidity (4.7 pH) of the body fluids of the insect is maintained to resist the growth of internal parasites and this is connected with the calcium metabolism of the insect. The predators which feed on the insect are defended against through the insects' secretory activity which is largely dependent upon the host. Leguminous hosts like *fleminga congesta*, *cajanus indicus* and *butea frondosa* are poor hosts from the point of view of the resin secreting efficiency of the insect. Insects fed on these hosts are helpless against the attack of predators like *E. amabilis* etc., whereas those on *shorea toluera* build thick and tough encrustations, which effectively protect them from their predatory enemies. Well fed insects maintained in a vigorous state of health can resist their enemies to a very large extent, through their defensive mechanisms of steady secretion of lac and incessant excretion of honey dew.

### 116. A note on the nitrogenous and fatty constituents of the blood of lac insects.

B. H. KRISHNA and M. SREENIVASAYA, Bangalore.

A method for the isolation of fats and proteins from insects has been described.

The globulin has been analysed and the nitrogenous constituents of the serum have been partitioned.

A comparatively high basic fraction characterises the serum component of the proteins from the lac insect.

The economic value of this investigation is indicated.

### 117. The determination of pyruvic acid in biological fluids in the presence of lactic acid, acetaldehyde and glucose.

B. H. KRISHNA, Bangalore.

The method of Krishna and Sreenivasaya (*Biochem. J.*, 1928, 22, 1169) has been simplified. Differences observed in the rates of oxidation of pyruvic acid and lactic acid, acetaldehyde, and glucose by ceric sulphate in acid solution permit of an electrometric titration of pyruvic acid in the presence of these substances.

The inflection point in the titration curve  $\frac{dE}{dv}$  against  $V$ , is taken as the end point.

The effects of dilution and hydrogen-ion concentration during titration both of which have a pronounced effect on the result, and the process of treatment preliminary to titration of biological fluids are discussed.



118. A microchemical study of the organic acids in healthy and spiked sandal leaves.

A. V. VARADARAJA IYENGAR, Bangalore.

Oxalic, malic, citric, succinic and tartaric acids were noted to be normally present in sandal leaves. Their relation to health and disease was studied.

119. A micro-method for the estimation of calcium in plants.

P. V. VARADARAJA IYENGAR, Bangalore.

A rapid and convenient method is described by which it is possible to estimate the amount of calcium occurring even in individual leaves.

120. Haemolysis by narcotics. Part I.—The haemolysis of red blood corpuscles by some primary and secondary amines and allied substances with reference to the hydrogen ion concentration of the solutions used.

K. C. SEN, Muktesar.

The substances used are methylamine, ethylamine, diethylamine, piperidine, ammonia and potassium hydroxide. When a comparison was made of the haemolytic powers of these substances with the hydroxyl ion concentration of the aqueous solution, a direct proportionality was observed. Thus with increase in the electrical conductivity of the solutions at the same dilution, the haemolytic efficiency also increased. Hence the pH of the solutions gave an indication of the lytic power of the substances. Since however the hydrogen ion concentration is the deciding factor in haemolysis in these cases, the important point of the permeability of these narcotics into tissues and cells has now to be considered in relation to their surface tension effects. A study of this appears to show that the lytic efficiency is more determined in these cases by the alkalinity or OH-ion concentration of the solutions than by their surface tension effects. A comparative study in this connection of the haemolytic efficiency of several fatty acids like formic, acetic, propionic, butyric, valeric and caproic acids also show that the hydrogen ion concentration is more effective than the surface tension effects in making the cell membrane permeable to haemoglobin.

121. The composition of the globulin of the Indian gram, *Cicer arietinum* by nitrogen distribution.

T. R. GOEL, L. S. NIGAM and H. N. BATHAM, Cawnpore.

- (1) The globulin of the Indian gram has been isolated and analysed.
- (2) The analytical results indicate that it contains the basic amino-acids, arginine, histidine, lysine and cystine.

122. Some aspects of the behaviour of cinchona alkaloids towards living cells.

N. D. KEHAR, Kasauli.

The behaviour of quinine bihydrochloride and quinine bisulphate was studied on the living cells of *Nitella* (*Characeæ*), regarding permeability and electrical conductivity. Interesting results have also been



observed with gelatin and agar-agar gels of definite concentrations, mixed with various inorganic salts that are supposed to be present in the living cells. Beautiful Liesegang rings are visible, showing remarkable differences with different salts of the alkaloid. An attempt has been made to correlate the physico-chemical and the bio-chemical aspects of the behaviour of these alkaloids on the cells in the system after quinine salts have been either injected or taken orally.

### 123. Polar adsorption in relation to Traube's surface tension rule.

SOCHINDRA NATH CHAKRAVERTY, Allahabad.

Traube's rule has been found to be in accord with many cases where the adsorption is not markedly polar. In order to find out whether a strongly polar adsorption would give the same series of adsorption isotherms as a non-polar one, the solutes and the medium remaining the same, a large number of experiments have been carried out with zirconium hydroxide as the adsorbent and some fatty acids as well as some amino-acids as the adsorbable solutes. It has been observed that stronger the acid is, the greater is its adsorption, and the chemical affinity existing between the surface of the adsorbent and the solute more than counterbalances any capillary effect. The adsorption series with formic, acetic, propionic and butyric acids is just the reverse of what we get in the Traube series. Almost similar results are obtained with amino-acetic, amino-propionic and amino-benzoic acids, where the acidic dissociation constant of the acids gives a comparative order of adsorbability when the same series of analogous solutes are considered. It is apparent therefore that in these cases Traube's rule is not obeyed due to the strongly polar nature of the adsorption.

### 124. Sensitisation of red blood corpuscles by bile salts, brilliant green and other substances and hemolysis by hydroxyl ions.

A. C. ROY, Allahabad.

In order to find out a possible explanation of the action of normal serum on the sensitised corpuscles, the present author has carried out a number of experiments with bile salts, soaps, dyes, etc. with the subsequent addition of low concentration of sodium hydroxide. It has been observed that by suitably sensitising the corpuscles, an almost permanent change occurs in the membranes of the red blood corpuscles which manifests itself by a greatly increased susceptibility to the presence of hydroxyl ions, and a rapid hemolysis occurs. From experiments on brilliant green it has been observed that the dye is adsorbed by the corpuscle membrane and it appears possible that the sensitising action of bile salts, soaps, etc. is due to the adsorption of these substances by the membrane of the red blood corpuscles. It appears also possible that the action of normal serum on the hemolysis of the sensitised corpuscles may be due to the alkali content of the serum.

### 125. The effect of some primary and secondary amines on red blood corpuscles sensitised by bile salts.

NARENDRA NATH MITTRA, Allahabad.

The hemolysis of red blood corpuscles can be carried out separately by bile salts as well as by different amines when the concentrations of these reagents reach a certain limit. When however, less amounts of these lytic agents are used, no hemolysis occurs. In certain cases



however a sort of sensitisation of the corpuscles can be observed when a low amount of any of these lytic agents is kept in contact with the corpuscles for some time and these sensitised corpuscles are then extremely susceptible to a slight addition of hydroxyl ions in any form. Rai in another communication has considered the case of sensitisation towards sodium hydroxide under certain conditions, and in this communication the author desires to present a large number of results of the effect, of several amines such as ethyl amine, diethyl amine, methyl-amine, etc. on the sensitised corpuscles. The concentration of the amines was varied to a great extent, in some cases a solution of strength M/10,000 being used, and the result shows that a very low concentration of the amines is quite an efficient hemolyser of the sensitised corpuscles whereas for the unsensitised corpuscles, an appreciably higher amount of the amines would be necessary for the hemolysis to take place. The general theory underlying the whole process of sensitisation has also been discussed.

#### 126. Nitrogen fixation by *Azotobacter Chroococcum* in soils in the presence of certain salts.

N. N. INUGANTI and K. HABIB HASAN, Hyderabad, Deccan.

Work was continued (Proc. Ind. Sc. Congress, Madras) to find out how far the nitrogen fixation is affected in soils containing salts of sodium, potassium and magnesium. In all these experiments pure cultures of *azotobacter* were inoculated and incubated at 37°C for a period of six weeks.

Few interesting observations were made as under :—

- (1) Sodium chloride does not affect the activity of the *azotobacter* even up to 2.5%, the highest amount of fixed nitrogen being when at 0.08% beyond which slight diminution takes place.
- (2) Sodium sulphate is only favourable when present in minimum quantity viz. 0.01%. When increased there is a gradual diminution in the nitrogen inasmuch as at 2.5% it is almost halved.
- (3) Potassium sulphate gives the highest quantity of fixed nitrogen when at 0.1% beyond which there is a slight diminution but even at 2.5% nitrogen is more than what is fixed when the salt is at .01% or .05%.
- (4) Potassium carbonate seems very favourable even at 2.5%. From the start viz. .01% to this degree the increase in nitrogen is very little and nothing appreciable. This varied proportion of the salt neither increases nor diminishes the activity of the organism.
- (5) Higher percentages of magnesium sulphate and magnesium carbonate diminish the activity of *azotobacter*, the most favourable being at .01% and .05% respectively.
- (6) None of these salts is found to destroy the activity of the organism even in higher percentages whereas in some cases it is increased and in others it is diminished.
- (7) In all trials it was found necessary to neutralise the acidity in order to maintain the degree of activity of the organisms.

#### 127. Chemical analysis of Standard Indian Cottons.

D. L. SEN, Bombay.

Quantitative determination of the various chemical constituents of eighteen standard Indian cottons of the three successive seasons, (1926-27, 1927-28, 1928-29) has been carried out.



The differences exhibited, between the three seasons, in each of the various constituents is discussed for each cotton, and also the differences, between the eighteen cottons, in each of the constituents for any one of the three seasons.

The practical significance of these chemical constituents in the process of dyeing, bleaching and spinning is also briefly discussed.

### 128. Influence of different reducing agents on one-bath chrome-liquor.

B. B. DHAVALÉ and G. N. PAL, Calcutta.

It was proved that:—

- (1) Even though a start was made with the same quantities of potassium bichromate and sulphuric acid, different reducing agents produced chrome-liquors of basicities varying widely from each other.
- (2) Irrespective of the different basicities produced by these different reducing agents, the contention that the absorption of chromium by the pelt increases with the increase in the basicity figure of the chrome-liquor is borne out.
- (3) From the examination of the leathers produced by these chrome-liquors, it is found that the organic reducing agents make the fibres more felty and the penetration of the dye deeper than the inorganic ones.

### 129. The Effect of addition of sodium chloride to chrome-liquor.

B. B. DHAVALÉ and G. N. PAL, Calcutta.

The effect of adding different amounts of salt to the chrome-liquor during chrome tanning was studied. Results obtained show that the addition of 5% salt on the pelt-weight leads to the highest absorption of chromium by the leather and as the use of this proportion happens to be the tanner's practice. The present investigation justifies by scientific experiments the empirical finding of the practical tanner. The comparative study of the qualities of the finished leathers obtained in the course of the investigation leads to the conclusion that it is advantageous to add about 5% salt to the chrome-liquor during tanning.

### 130. Effect of sodium chloride on lime-liquor.

B. M. DAS and U. N. DUTT, Calcutta.

Investigations were carried out to study the effect of adding salt to the lime-liquors in the manufacture of leather. Results obtained show that salt increases the swelling of the hides in lime-liquor and also helps in the production of a leather having tighter and finer grain.

### 131. On the use of zinc chloride in tanning.

B. M. DAS and U. N. DUTT, Calcutta.

Investigations were made to find out the effects of zinc chloride in the soaking and pickling processes in connection with the manufacture of chrome box sides. The results show that a finer and tighter grained leather is obtained by the zinc chloride treatment.



**132. On the resistance of shellac films from various varnishes to the action of water and chemicals.**

**M. VENUGOPALAN and M. RANGASWAMI, Ranchi.**

In continuation of a study of the advantages of employing mixed solvents for shellac varnish, an examination of the films from solutions in some mixed solvents has been instituted.

The effect of water, brine, acid, alkali and a few gases on the appearance and structure of films from different varnishes has been discussed. Different films possess different capacities for water absorption but the effect on the appearance and structure of the films are in all cases only temporary. Brine, acids and the gases experimented with have no effect on the films and immersion in dilute alcohol, very little. A strong alkali, however, has been found to destroy the film in all cases to a smaller or greater extent.

In the various tests, mixed solvents have generally been found to give better films than single solvents and mixtures of methyl alcohol or ethyl alcohol with acetone have been observed to offer the greatest resistance to the action of water and chemicals tested.

**133. A preliminary survey of the problem of fuel economy in the United Provinces.**

**N. G. CHATTERJI, Cawnpur.**

The investigation has the following objects :--

1. General economy in coal consumption in factories to reduce the fuel bill.
2. Prevention of atmospheric pollution by smoke from factory chimneys.
3. To replace wood by coke as domestic fuel, for the conservation of forests or for their utilisation for more useful purpose.
4. To find a suitable substitute with proper distribution organisation of the cowdung cake fuel.

**134. Mond gasification of water-hyacinth.**

**H. K. SEN and H. N. CHATTERJEE, Calcutta.**

In view of the possible commercial utilisation of the weed by gasification, experiments have been undertaken to critically examine its suitability in this direction. Gasifying at  $600^{\circ}$  in the presence of air saturated with water vapour at  $65^{\circ}$ , the maximum quantity of ammonium sulphate per ton of air dry hyacinth has so far been 82 lbs. only. The economic aspect is also discussed.

**135. The Utilisation of Wood Tar.**

**Y. K. RAGHUNATHA RAO, Bangalore.**

Attempts have been made to utilise the wood tar from the Mysore Iron Works in different ways. It has been found that on a small scale, lamp-black of good quality can be produced but the burning of the tar on a larger scale offers considerable difficulty. It appears better to utilise only certain fractions for this purpose.

The pitch can be utilised to some extent as a paint and the phenolic bodies yield interesting formaldehyde condensation products.

In conjunction with Mr. B. Sanjiva Rao an examination of the constituents of the tar has been undertaken and numerous complex substances found to be present in it.



## 136. Studies in the Michael's Reaction.

UMA PRASANNA BASU, Calcutta.

An investigation into the mechanism of the condensation between cyanoacetamide and  $\beta$ -diketones is being made and certain results have already been obtained which indicate that in all such reactions it is the ethylenic linkage formed by the isomeric change of the  $\beta$ -diketones into their enolic modifications which is responsible for the initial condensation, and consequently this view supports the general principle that in

a conjugated system of the type  $\begin{array}{c} | \\ -C=CH-C=O \\ | \end{array}$ , the ethylenic linkage is more reactive than the carbonyl.

Ethyl 3-cyano-6-methyl-2-pyridone-4-carboxylate was obtained by condensing sodio-cyanoacetamide and acetone-oxalester both in alcoholic solution and in ethereal suspension. That the reaction takes place through the enolic phase is evident from the fact that *o*-ethyl-acetone-oxalester, Et. COO. C(OEt)=CH. CO. Me, also gave rise to the same product. Similarly 3-cyano-4-phenyl-6-methyl-2-pyridone was obtained by condensing *o*-methyl-benzoylacetone, Ph. C(OMe)=CH. CO. Me, with sodio-cyanoacetamide. Certain other interesting observations have been made from an attempt to ascertain the position of the sodium atom in the condensation product between acetyl-acetone and sodio-cyanoacetamide. It is now found that the Michael product is the N-Na salt of 3-cyano-4:6 dimethyl-2-pyridone. Consequently by condensing acetyl-acetone with sodio-cyanoacet-methyl-amide, the condensation product N-methyl-3-cyano-4:6-dimethyl-2-pyridone was directly obtained as was also derived from the methylation of the sodium salt of the former compound. A probable mechanism of the reaction has been suggested, which again indirectly supports the much criticised Thiele's theory. Further work is in progress.

## 137. Synthesis in the Thiazole Series.

INDU BHUSAN SEN-GUPTA, Calcutta.

The interaction of aniline and other aromatic amines with monochloro-acetyl chloride leads at first to the corresponding amide, which, on being treated with potassium sulphocyanide in alcoholic solution gives two products of the composition—

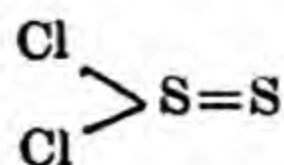


These may be regarded as having been derived from two forms of potassium sulphocyanide. Experiments to convert them into closed ring compounds are in progress.

## 138. Studies in organic polysulphides. Part I.

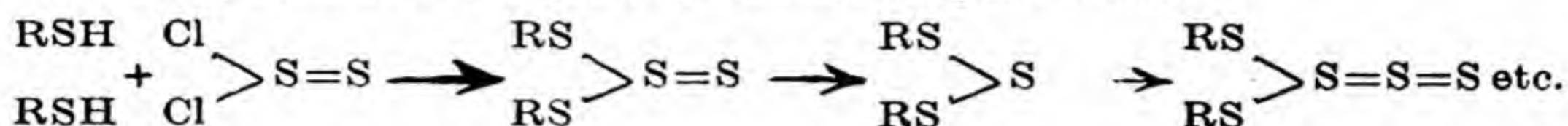
INDU BHUSAN SEN-GUPTA, Calcutta.

Interaction of mercaptans and  $S_2Cl_2$ , generally gives rise to a mixture of  $R_2S_2$ ,  $R_2S_3$ ,  $R_2S_4$  and  $R_2S_6$ , in which  $R_2S_3$  predominates. The alkyl and aryl derivatives of this type have been prepared, the former being high boiling liquids, and the latter crystalline solids having sharp melting points.  $R_2S_3$  may also be derived by the action of R.S.Cl and  $Na_2S$  in ethereal or chloroform suspension in a practically pure condition.  $R_2S_4$ , and  $R_2S_5$ , have similarly been prepared from  $Na_2S_2$ , and  $Na_2S_3$ , respectively. This implies the probable existence of  $S_2Cl_2$ , mainly in the form

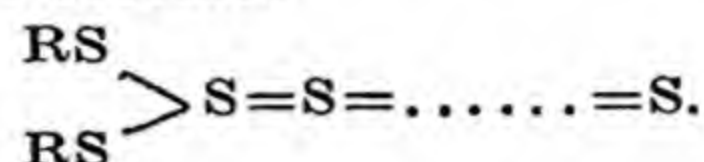




and the different polysulphides are therefore derived from the addition of different quantities of sulphur to the end sulphur atom:—



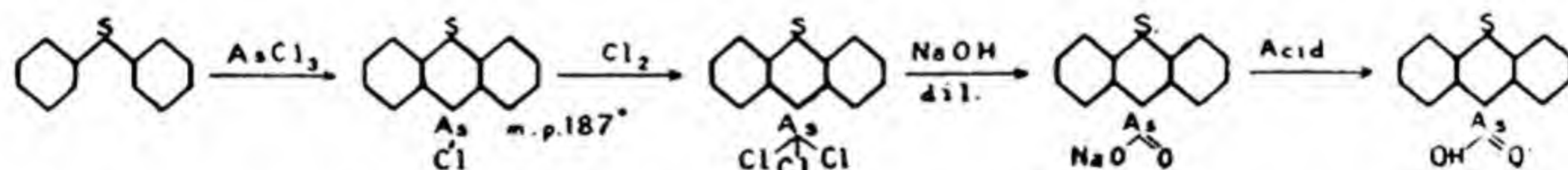
The alternate constitution  $\text{Cl-S-S-Cl}$ , for sulphur monochloride would require the union of the various alkyl or the aryl radicals through a chain of sulphur atoms from which the various polysulphides are derivable by rupture of the chain and subsequent reunion; preference therefore is given to the former constitution for sulphur monochloride, and consequently that of the polysulphides becomes



### 139. Thioarsines.

INDU BHUSAN SEN-GUPTA, Calcutta.

The great therapeutic value of sulphur and arsenic led to an attempt to synthesise derivatives containing both these elements in suitable positions with respect to each other. Whilst the pharmacological investigations await, the following reactions have been realised; by heating equimolecular quantities of the sulphides and arsenic trichloride to about  $200^\circ$  in an oil-bath, for about an hour a brown solid mass is left behind which on crystallisation from carbon tetrachloride and acetylene tetrachloride is obtained in well-defined crystals with definite melting points:—



Similar derivatives have also been obtained from naphthyl and nitrophenylsulphides, etc.

### 140. The Photo-chemical and dark reaction between bromine and organic hydroxy-acids in presence of potassium bromide.

J. C. GHOSH and R. M. PURKAYASTHA, Dacca.

It has been observed that—

- (1) the dark reaction between pure bromine and organic acids like phenyl-lactic acid, mandelic acid and lactic acid (a) is bimolecular even when the organic acid is in large excess, (b) becomes monomolecular in presence of potassium bromide.
- (2) the photo-chemical reaction between pure bromine and the above acids (a) is monomolecular when the acids are in large excess, (b) becomes zero-molecular in presence of potassium bromide.

An attempt has been made to explain this remarkable diminution in the order of reaction under the influence of (a) light, and (b) potassium bromide.



## 141. Raman Effect in Fused Naphthalene.

N. G. MITRA and D. L. SHRIVASTAVA, Lahore.

Raman spectra has been taken using naphthalene in the fused state. The frequency changes found, follow in general those obtained by other workers with naphthalene in organic solvents.

## 142. Relation between the intensity and the velocity of the reaction between sodium nitrite and iodine in visible and infra-red radiations.

A. K. BHATTACHARYA and N. R. DHAR, Allahabad.

It has been observed that the relation between the velocity of a reaction and the intensity of the incident radiation can vary from any proper fraction to 2 depending on the ratio of the thermal and photo-chemical velocities of the same reaction. In the case of the reaction between sodium nitrite and iodine the relation between velocity and intensity varies from  $1/3$  to  $3/2$ . In order to accelerate the dark reaction a very small amount of potassium iodide was used in dissolving the iodine. Both sodium acetate and borax were used as buffer solutions.

The absorption of the incident radiation has been determined by a radiomicrometer. The amount of radiation absorbed is directly proportional to the intensity of the incident radiation.

## 143. Chemical reactions in infra-red radiations.

A. K. BHATTACHARYA, Allahabad.

The kinetics, temperature co-efficients and quantum efficiency of several chemical reactions have been investigated under the influence of radiations of mean wave-lengths  $7,304 \text{ \AA}$ , using Wallace M and S filters and in light using solution filters (saturated dichromate solution kept in a cobalt glass cell 1 cm. thick).

The changes in the reactions studied were determined either by suitable titrations or spectrophotometric measurements.

The temperature co-efficients of all these reactions (wave-lengths  $7,304 \text{ \AA}$  and  $8,000 \text{ \AA}$ ) are less than those of the corresponding dark reactions. The quantum efficiency of all these reactions usually increases with increasing temperature.

Measurements of extinction co-efficients show that all radiations of wave-length from  $4,400 \text{ \AA}$  to  $7,000 \text{ \AA}$  are absorbed by the reacting systems and thus they are accelerated by the absorption of the incident radiation.

## 144. Experiments in photosynthesis.

G. GOPAL RAO, N. R. DHAR and SANYAL, Allahabad.

While repeating some of the experiments of (J. Phys. Chem. **29**, 926, 1925) on the photosynthesis of formaldehyde we found that a solution of methylene blue, through which a current of dry carbon dioxide was passed, while exposed to sunlight, became slightly less intense in colour than a similar solution exposed to the sun but through which no carbon dioxide was passed. It was suspected that some of the methylene blue might have been oxidised by carbon dioxide in presence of light. Suspensions of chlorophyll in water showed a behaviour exactly similar to that of methylene blue solutions. It was recalled that Chakravarthi and Dhar (Z. anorg. Chem. 1925) had shown that certain dyes can act as reducing agents under suitable conditions. On the subsequent experiments a current of dry carbon dioxide was passed through a solution of methylene blue or a suspension of chlorophyll exposed to light from a 500 watt gas-



filled tungsten filament lamp and the issuing gas tested for carbon monoxide by the iodine pentoxide method. Small quantities of carbon monoxide were always detected. Comparison with blank experiments showed that the amount of carbon monoxide found is considerably higher in the presence of chlorophyll and methylene blue than in their absence. We, therefore, conclude that, besides its photo-sensitising action, chlorophyll also exerts a slight reducing action. These facts are calculated to throw considerable light on the carbon assimilation by plants.

145. Photo-chemical oxidation of salts of some organic acids, lecithin, cholesterol and some food materials by air.

C. C. PALIT, Allahabad.

1. Aqueous solutions or suspensions of the following substances have been oxidised by passing air in presence of sunlight:—sodium formate, sodium tartrate, lecithin, cholesterol, butter, milk, egg-white and egg-yellow.

2. Zinc oxide acts as a photo-sensitiser in the oxidation of sodium tartrate and formate.

3. Photo-chemical oxidation of glucose, starch, glycogen, glycine,  $\alpha$ -alanine, hippuric acid, urea, sodium urate, formate, tartrate, potassium stearate and oleate is markedly increased in presence of ferric nitrate and uranium nitrate.

4. Dilute solutions of lactic acid, oxalic acid, tartaric acid and citric acid are appreciably oxidised by air in presence of sunlight and the order in which they are oxidised is:—oxalic > lactic > tartaric > citric.

5. Experimental results on the estimation of carbon dioxide prove that glucose, glycine, potassium oleate, lecithin, cholesterol, butter, etc., are oxidised by air in presence of sunlight chiefly to carbon dioxide and not to any intermediate product.

6. Our experimental results show that the amount of oxidation increases with (i) the amount of light falling on the solutions, and (ii) the time of exposure.

7. Comparative experiments show that the order in which the food materials are oxidised in presence of sunlight is as follows:—egg-yellow > starch > egg-white, butter > glucose.

8. Einstein's Law of Photo-chemical Equivalence is approximately applicable to the photo-chemical oxidations of glucose, lactose and alanine by air.

9. Experimental results show that appreciable amounts of the compounds of the peroxide type are formed when air is passed through aqueous suspensions of cholesterol, olive oil and butter. Moreover appreciable amounts of glucose have been oxidised by mixing the solution of glucose with exposed cholesterol, olive oil and butter containing the peroxide compounds. Hence it is believed that the antirachitic and beneficial properties of substances not containing the necessary vitamins are due to the presence of peroxides which help the oxidation of food materials in the animal body.

146. Photolysis of potassium-cupri-oxalate.

W. V. BHAGWAT and H. L. DUBE, Allahabad.

It has been observed in this laboratory that a solution of potassium-cupri-oxalate is decomposed in light and the velocity of this photo-chemical reaction is greatly accelerated by ferric and uranyl salts.

We have carried on quantitative experiments on this reaction. In presence of ferric chloride, the velocity of the photochemical decomposition of potassium-cupri-oxalate appears to be zero-molecular in sunlight and is independent of the concentration of the photolyte. An



excess of potassium oxalate has little influence on the reaction. Similar results have been obtained by Allmand and Webb (J. Chem. Soc., 1518, 1929) in the photolysis of potassium-ferri-oxalate.

#### 147. Photodecomposition of nitrous acid.

K. S. MURTI, Allahabad.

Solutions of nitrous acid decompose in darkness at the ordinary temperature. In presence of light the decomposition is greatly accelerated. In bright sunlight, the velocity of decomposition in open vessels is approximately three times that in the darkness and that in the total light from a 1000 watt tungsten filament lamp is a little more than two times the velocity of decomposition in the dark.

It appears that the temperature coefficient of the photochemical decomposition is greater than unity.

The velocity of decomposition increases with the increase of the initial concentration of nitrous acid.

In all these reactions, the velocity constant follows the unimolecular formula.

Experiments on the quantum yield with the different wavelengths and at different temperatures, and on the variation of velocity with the pressure of nitric oxide in the reaction vessel are in progress.

#### 148. Chemi-luminescence in the oxidation of fluorescent and non fluorescent substances by hydrogen peroxide and ozone.

N. N. BISWAS, Allahabad.

1. When numerous fluorescent and non-fluorescent dye solutions are oxidised by hydrogen peroxide and ferrous sulphate, a glow, which is visible in a dark room, is observed

2. The wave lengths of the radiations given out in the glow obtained in the oxidation of some fluorescent dyes, by ozonised oxygen have been measured.

3. Silica containing small quantities of neutralised dyes in the adsorbed state when suspended in ethyl alcohol and ozonised oxygen is passed through the suspension a glow is observed.

4. When small amounts of a dye, which gives out good glow, are mixed with another dye of which the glow is feeble, the resulting glow obtained by passing ozone, is more intense than that obtained with the dye yielding feeble glow.

5. Increase of temperature of the reacting substances leads to the intensification of the glow in the oxidations of reducing agents by ozone or hydrogen peroxide.

6. Increase of concentration of the reducing agents causes an increase of the intensity of the glow up to a limiting value; if the concentration is increased further, the glow becomes feeble and finally stops.

#### 149. Photochemical activity of tungstic and molybdic acid sols.

A. K. BHATTACHARYA and S. GHOSH, Allahabad.

Several years ago Wessiljewa (Z. wiss. phot. 1913, 12, 1) found that tungstic acid sol when freshly prepared can be reduced to blue coloured lower oxide by reducing agents like glucose, formaldehyde, alcohol, etc., and that this reduction is photosensitive. On ageing tungstic acid loses its photosensitivity remarkably, and it can be regained by heating the sol. We have ascribed this behaviour of tungstic acid to the polymerisation of this substance on ageing, and evidence to this fact has been



obtained by conductivity and viscosity measurements. We have now determined the effect of monovalent cations on the photochemical activity of tungstic acid sol and it is found that cations decrease the photosensitivity and are in the following decreasing order:—

$\text{Rb}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ . The concentrations of the added cations are less than their precipitating concentrations. It is interesting to note that the coagulating powers of different monovalent cations are in the same order as the effect of the cations on the photosensitivity of the tungstic acid sol.

We have found that molybdic acid sol obtained by the interaction of ammonium molybdate and hydrochloric acid is also photochemically active when reduced by alcohol, grapesugar, etc., and this property slightly diminishes when the sol is allowed to age, which can be regained by heating the sol. The monovalent cations decrease the photochemical activity in the following decreasing order:— $\text{Rb}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ .

In one of our publications we have shown that the coagulating powers of different cations are also in the above order. Moreover, we have shown that molybdic acid sol contains appreciable amount of the substance in the molecular condition, which gradually polymerises on ageing.

The rate of reduction of tungstic and molybdic acids by reducing agents has been measured spectrophotometrically.

#### 150. A new photo-tropic compound.

G. SAMBAMURTI and N. L. NARASIMHAM, Rajahmundry.

A photo-tropic compound of the composition  $\text{I.Hg.S.S.S.Hg.I}$  has been obtained with a bright yellow colour, which rapidly changes through green to grey on exposure to light, the colour, returning in the dark pretty quickly. The products of decomposition when brought into intimate contact have not produced the compound.

#### 151. Studies in Triboluminescence.

S. S. BHATNAGAR, K. G. MATHUR and K. L. BUDHIRAJA, Lahore.

Triboluminescence of arsenious trioxide and saccharine have been studied in some detail. A method for the quantitative measurement of the intensity of triboluminescence has been described. Fresh crystals of  $\text{As}_2\text{O}_3$  have been found to rapidly lose their triboluminescent properties when exposed to a strong beam of ultra-violet and X-rays. The temperature and the viscosity of the crystallising solution have also been found to have considerable influence on the triboluminescent properties of the crystals and an explanation based on the possible separation of the supersaturated phase has been suggested.

#### 152. Slow and induced oxidation of glycogen, lecithin, cholesterol, formate, oleate, stearate and some food materials.

C. C. PALIT, Allahabad.

1. An aqueous solution of sodium formate and an aqueous suspension of glycogen has been oxidised by air at  $25^\circ$  in presence of caustic soda, sodium bicarbonate and different metallic hydroxides.

2. The oxidation of glycogen is retarded by fats and nitrogenous substances.

3. The induced oxidation of potassium stearate and oleate by air is retarded by carbohydrates and to a greater extent by a mixture of carbohydrate and urea.



4. The oxidation of carbohydrates by hydrogen peroxide and ferric sulphate is retarded by glycine potassium stearate and oleate.

5. Experimental results on the estimation of carbon dioxide prove that glucose, glycine, potassium oleate, lecithin, cholesterol, milk, egg-yellow and egg-white are oxidised by air at 25° in presence of inductors chiefly to carbon dioxide and not to any intermediate product.

6. Comparative experiments have been carried on the induced oxidation of fats, carbohydrates and nitrogenous substances to prove whether nitrogenous matter is more readily oxidised than carbohydrates. The results show that in neutral solutions with cerous hydroxide as an inductor, the order in which the oxidation takes place is as follows:—Egg-white > egg-yellow > starch > glucose > butter. This order is the same as stated by Voit, the eminent physiologist, from physiological experiments.

7. These results on slow and induced oxidation of fats, nitrogenous substances and carbohydrates occurring either singly or in mixtures by air at the ordinary temperature are important, because these oxidations are of the same type as those taking place in the animal body.

### 153. Induced oxidation of carbohydrates and fats by passing air in presence of phosphorus.

S. N. CHAKRAVARTI, Allahabad.

1. Finely divided phosphorus has the greatest capacity of oxidising carbohydrates and fats, colloidal phosphorus comes next and small bits of phosphorus comes last.

2. In all cases excepting that of colloidal phosphorus the oxidation increases with time. In the case of colloidal phosphorus the amount of oxidation does not vary much with time.

3. It appears from my results that amongst the carbohydrates starch is oxidised to the greatest extent.

### 154. Period of induction in chemical reactions, Part III. Interaction of alkali iodates and hypophosphorous acid.

P. NEOGI and BENOYENDRA NATH SEN, Calcutta.

A distinct period of induction has been observed in the interaction of hypophosphorous acid and iodates which takes place in successive stages. The phenomenon has been studied with reference to light, temperature, dilution, action of acids, salts, alcohols and other substances. The velocity of the reaction has been measured and the successive stages ascertained from conductivity measurements. An interesting phenomenon is observed in the difference of the effects of isomeric alcohols like *n*-propyl and *iso*-propyl alcohols on the period of induction which might advantageously be utilised in differentiating the two isomeric alcohols.

### 155. The system-lithium hydroxide and oxyacids of phosphorus.

P. NEOGI and BENOYENDRA NATH SEN, Calcutta.

The progressive neutralisation of the oxyacids of phosphorus with lithium hydroxide has been studied electrometrically and the different phases studied with reference to the various compounds formed.



## 156. Chemical reactions under electrodeless discharge.

S. S. BHATNAGAR, R. K. SHARMA *and* N. G. MITRA,  
Lahore.

Various photo-chemical and other reactions have been tried under the electrodeless discharge with a view to study their mechanism. It has been found that some photo-chemical reactions follow the same trend as they do in light while the change observed in other reactions is quite different.

## 157. Chemical reactions under electrodeless discharge.

N. A. YAJNIK, R. K. SHARMA *and* M. C. BHATNAGAR,  
Lahore.

The action of electrodeless discharge on a number of substances has been tried and it has been found that most of them are decomposed in a peculiar way. The phosphates and carbonates were found to be very stable towards the discharge and were not found to undergo any decomposition even on prolonged exposure.

It was also observed that in case of certain polymorphic substances, one modification was found to change into another under the influence of the electrodeless discharge.

## 158. Velocity of ionic reactions. Part IV.

A. N. KAPPANNA, Nagpur.

The paper deals with the kinetics of the reaction between sodium formate and potassium permanganate in neutral solutions. With only the reacting salts in neutral solutions, velocity measurements show that the reaction does not proceed in a simple manner. This has been found to be due to the variation in total ionic strength with the progress of the reaction. Velocity measurements have been made in the region  $0.001\omega - 0.05\omega$  total ionic strength to examine the range of validity of Debye-Huckel limitation equation.

## 159. On the neutral salt effect: The activity coefficient of hydrogen ions in mixtures of phosphoric acid and electrolytes.

SUBODH KUMAR MAJUMDAR, Calcutta.

The effect of different concentrations of potassium chloride, potassium bromide, potassium iodide and potassium sulphate on the activity coefficient of hydrogen ions in phosphoric acid solutions has been studied. Sulphates diminish hydrogen ion concentrations very markedly, while the halides show slight reverse effect. These effects have been discussed from different view points. The effect of dilution as also the addition of neutral salts have been studied in the light of the Debye and Hückel Equation and certain conclusions regarding the ionisation of phosphoric acid arrived at.

## 160. A contribution to the study of heterogeneous reactions.

D. D. KARVÉ.

The reaction between carbon disulphide and aqueous solutions of sodium hydroxide is a well-known heterogeneous reaction, in which the chief product of decomposition is sodium trithionate  $\text{Na}_2\text{CS}_3$ . It has been found that if hydrogen peroxide is present along with the alkali,



the trithionate is oxidised rapidly and various products including sulphite, sulphate, carbonate and free sulphur are produced. By using standard conditions (*e.g.* constant rate of shaking, constant rate of passing drops of carbon disulphide through the alkali etc.) and varying the concentrations of alkali as well as peroxide, the rate of the reaction (*i.e.* the using up of the alkali) has been determined and conclusions drawn as regards the mechanism of the reaction.

### 161. The solubility of formaldehyde in organic solvents.

D. D. KARVÉ.

In connection with certain condensation reactions that are being carried out, it was necessary to use a solution of formaldehyde in various organic solvents. Solubilities in nitrobenzene, aliphatic and aromatic hydrocarbons as well as carbon disulphide were determined by passing a stream of formaldehyde gas into the solvent until saturation was reached and estimating the aldehyde by oxidation to formic acid and titration with standard alkali. Partition coefficients of formaldehyde between water and organic solvents have also been determined.

### 162. Sodium aluminate solutions. Part I.

S. M. MEHTA and N. G. JOSHI.

Electrical conductivities of solutions containing  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  in different ratios have been measured at  $30^\circ\text{C}$  and for concentrations ranging from 0.2N to 2N. The equivalent conductivity-normality curves show that for a given ratio of  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ , the conductivity increases with dilution, as expected, due to the increased hydrolysis.

The curves obtained by plotting the equivalent conductivity against the ratio of  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$  give a sharp maximum at the point corresponding to the ratio  $2\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ . It appears that a salt corresponding to this ratio exists in solution and that the other ratios are, probably, mixtures of this with  $\text{NaOH}$ .

Further work on the determination of pH of these solutions is in progress.

### 163. A method for distinguishing isomeric, tautomeric, and polymeric from polymorphic optically active substances.

BAWA KARTAR SINGH, Cuttack.

A chemical substance may exist in two (or more) mutually convertible modifications. The difference between them may be due to isomerism (including tautomerism) or polymorphism. The solutions of isomeric substances will be different (unless tautomeric equilibrium has been established), whereas polymorphous substances will give identical solutions.

In this paper a new method for the diagnosis of polymorphous and isomeric modifications of optically active substances based on the above mentioned distinction is described. The rotatory power of the polymorphous modifications will be identical, whereas it will be different for isomeric or tautomeric forms. It is, however, possible for the rotatory dispersion curves of two different substances to intersect at a point corresponding to some wave length and thus indicate identical rotatory power for that wave length. The result will be that the modifications which are isomeric will appear as polymorphous. It is, therefore, suggested that the rotatory dispersions over a wide range should be measured. The value of the rotatory dispersion of the polymorphous modifications



will be constant, whereas this will vary for isomeric substances. *o*-iodo-phenyl-imino-d-camphor occurs in three forms melting at 86–87°, 93°, and 96–97° respectively. The value of the rotatory dispersion for the three forms is identical, which shows that they are polymorphous and not stereoisomeric.

#### 164. Studies in optical rotation.

S. M. PATEL and P. C. GUHA, Bangalore.

Organic compounds showing high molecular rotation have been prepared by Forster (J.C.S., 1909, 95, 942; 1919, 115, 889; 1921, 119, 789) and Singh (J.C.S., 1919, 115, 980, 1599; J. Ind. Chem. Soc., 1926, 3, 389) by condensing camphorquinone with aromatic diamines. Camphorquinone has now been condensed with *p-p*-diaminodiphenylurea, -thiourea, and -oxamide, as also with thiocarbohydrazide; and all of the resulting compounds excepting the last have been found to possess high molecular rotations (*viz.*) +8911°, +7652°, +9141°, and +1556° respectively, in chloroform.

Further work involving the use of diaminodinaphthyl urea, -thiourea, and -oxamide, instead of the corresponding phenyl compounds, as also the study of rotations of the compounds obtained from aminocamphor and aromatic diketones and dialdehydes, is in progress.

#### 165. The electrical conductivity in a gas subjected to ionisation by collision.

SHRIDHAR SARVOTTAM JOSHI, Benares.

On an analysis of the current voltage relationships in a discharge tube filled with a simple gas subjected to ionisation by collision due to fields such that their radiational effects in the space can be neglected, the following approximate equation has been theoretically deduced,

$$N = aU/Z.$$

where, *N* is the number of ionic pairs per c.c., *a* denotes the number of fresh ions produced by collisions with an electron during one centimeter of its path, *U* is the electronic velocity in the direction of the applied field, and *Z*, the co-efficient of ionic recombination.

#### 166. On the adsorption of gases by solids.

ASHUTOSH GANGULI, Calcutta.

The well known adsorption formula of Langmuir,

$$c = \frac{k\eta}{1 - \eta\beta}$$

(where *c* is the concentration, *η*, the amount adsorbed, being reciprocal to surface area *Ω* covered by the adsorbed substance, *K* is Langmuir's constant) has been modified by Volmer, who obtained thermodynamically

$$C = \frac{k\eta}{1 - 2\eta\beta}$$

by using a modified equation of state  $\pi(\Omega - \beta) = RT$ , *π* being the surface tension and *β* van der Waals correction. In a previous communication Ganguli and Kar have deduced Langmuir's equation by statistical



mechanics and have attributed a physical meaning to Langmuir's constant. Thus

$$k = \frac{(2\pi MRT)^{\frac{1}{2}}}{\rho \cdot N} e^{-\frac{a}{RT}},$$

where  $M$  is the molecular weight of the adsorbed substance  $N$  Avogadro Number,  $a$ =adsorption potential and  $\rho$  is a constant, which reduces to  $h$  for uni-molecular adsorption layers. 'a' has been identified with the heat of adsorption and also to the heat of sublimation of the adsorbed substance in several cases. This again corresponds with the maximum value of Polanyi's adsorption potential (for uni-molecular adsorption layers). The calculated values of  $K$  agree remarkably well with the experimental values. Since adsorption potential is equal to heat of sublimation in most cases, adsorption may be regarded as a process of condensation on the surface, the adsorbed substance being present as a layer of solid on the surface of the solid adsorbent. Volmer's method has been criticised because he combines thermodynamics with Kinetic theory, and a correction in the Gibbs-Thomson equation has been suggested. The modified equation is

$$n = \frac{1}{\left(\frac{1}{\eta} - \beta\right)} = -\frac{c}{RT} \frac{d\gamma}{dc},$$

where  $\gamma$ =surface tension,  $c$  the concentration,  $\eta$  and  $\beta$  have the same significance as before.

167. On the minimum electrical fields for a chemical change in a gaseous medium. Part I. The decomposition of nitrous oxide.

SHRIDHAR SARVOTTAM JOSHI, Benares.

In the now considerable literature on reactions produced under various types of electrical discharge, no quantitative data are available for the minimum potentials necessary to initiate chemical changes in gaseous media. Such measurements are, however, necessary for any comprehensive theory of these reactions. The present paper gives results for the decomposition of nitrous oxide. The apparatus consisted of two glass tubes sealed together as in the familiar Siemens' ozoniser. The applied potential alternating at a given frequency is increased gradually till decomposition just set in. From this, and from a knowledge of the capacities of the various dielectrics in the reaction vessel, the intensity of the electrical field developed at the inner surface can be calculated for any given gas pressure. In a number of cases these values have been found to be less than the corresponding dielectric strengths, for which an explanation has been suggested.

168. The 'Corona pressure' phenomenon under electrical discharge in Siemens' ozoniser.

SHRIDHAR SARVOTTAM JOSHI, Benares.

It was observed that an instantaneous pressure rise of about 2 cms. was produced just on the application of a high alternating P.D. (about 40,000 volts r.m.s. per cm.) to a Siemens' ozoniser, filled with a number of well purified gases, and also such gaseous mixtures as did not change chemically under the influence of the discharge. The subsequent pressure rise was much slower. An equal, and a similarly instantaneous pressure fall, followed by a slower change, was noticed as the applied P.D. was switched off. The initial, 'Corona' pressure rise was found



to increase regularly with the gas pressure at a constant P.D. over a limited pressure range. It varies similarly with, (i) the magnitude of the applied P.D., (ii) the ionisation current in, and (iii) the energy dissipated in the discharge space. Experiments are described in order to examine whether the initial pressure change is a thermal or an electrical effect.

### 169. Surface tension of sols in presence of electrolytes.

D. N. CHAKRAVARTI, Nagpur.

In series of previous papers it has been established that when small quantities of electrolytes are added to a sol there is an appreciable fall in the viscosity. In this paper it has been found that surface tension of sols increase when small quantities of electrolytes are added. This increase in surface tension is due to the increase in the charge on the sol by the adsorption of ions carrying the same charge as the sol. The increase in the charge on the sol is associated with the decrease in the hydration and viscosity and increase in the surface tension. On the other hand when greater quantities of electrolytes are added the adsorption of ions carrying the opposite charge is more prominent than the adsorption of ions carrying the same charge, consequently the charge on the sol is decreased and hence the hydration will increase and surface tension decrease with increase in concentration of electrolytes until coagulation point is reached.

### 170. Surface tension of solutions of electrolytes of different concentrations and at higher temperatures.

K. P. CHATTERJEE, Allahabad.

Systematic investigation is being made in the surface tension of certain electrolytes, specially of saturated solutions of these. Apparatus for dealing with saturated solutions has been devised and the method of capillary rise is used.

With sodium chloride, the following results have been obtained.

Temperature.	Grams of sodium chloride with 100 grams of water.				Saturated solution of sodium chloride.
	0 gram.	10 grams.	20 grams.	30 grams.	
40°	69.5	72.3	74.8	77.6	79.3
50°	67.8	70.6	73.3	76.2	77.9
60°	66.0	68.8	71.6	74.6	76.6
70°	64.2	67.2	70.0	73.1	75.3
80°	62.4	65.3	68.3	71.4	73.8
90°	60.5	63.4	66.5	69.5	72.4

Surface-tension increases with increase of concentration in a practically linear manner, but the value of the increment is not the same at all temperatures. With increase of temperature, this value seems slightly to increase.

With rise of temperature, surface tension decreases in the usual way.



**171. Viscosity of solutions of electrolytes of different concentrations and at higher temperatures.**

K. P. CHATTERJEE, Allahabad.

A special apparatus has been devised for the investigation of viscosity of saturated solutions. Incidentally, solutions of other concentrations have also been investigated.

With sodium chloride the following results have been obtained.

Temperature.	Grams of sodium chloride with 100 grams of water.				Saturated solution of sodium chloride.
	0 gram.	10 grams.	20 grams.	30 grams.	
40°	·00658	·00758	·00950	·01160	·013245
50°	·00554	·00667	·00800	·00970	·011210
60°	·00475	·00568	·00690	·00840	·009556
70°	·00414	·00495	·00600	·00720	·008390
80°	·00365	·00440	·00535	·00640	·007413
90°	·00326	·00391	·00478	·00570	·006621

With greater concentration, greater becomes the increment of viscosity, but the values decrease with rise of temperature.

Various formulæ have been discussed.

Potassium chloride has also been investigated.

**172. Aromatic disulphides and Sugden's parachor.**

S. S. BHATNAGAR and BALWANT SINGH, Lahore.

Parachors have been calculated for a number of aromatic disulphides from their surface-tension values, determined in the fused state. The observed parachors are in good agreement with those calculated from the atomic and structural constants of Sugden. From these values the constitution of the disulphides has been derived.

**173. Mercaptans and Sugden's parachor.**

S. S. BHATNAGAR, BALWANT SINGH and RAM SINGH, Lahore.

Parachors have been calculated for a number of mercaptans from their surface-tension values, determined in the fused state. It has been shown that the mercaptans are not associated, while the corresponding alcohols and phenols are highly associated in the liquid state.

**174. Influence of magnetic field on the adsorption of electrolytes by fine insoluble precipitates.**

MATA PRASAD and R. K. VALVEKAR, Bombay.

Adsorption of ferric chloride by ferric oxide, manganese dioxide and barium sulphate; of potassium permanganate by manganese dioxide, ferric oxide and barium sulphate; of copper sulphate by copper oxide, manganese dioxide and barium sulphate and of potassium chromate by lead chromate, ferric oxide and chromium oxide has been studied.

The results obtained show that the magnetic field influences the process of adsorption to a great extent. The amount of adsorption is



either increased or decreased by the magnetic field according to the magnetic nature of the adsorbent and the substance adsorbed.

175. Influence of magnetic field on colloidal solutions.

MATA PRASAD and R. K. VALVEKAR, Bombay.

The influence of magnetic field on colloidal solutions of (i) positively and negatively charged ferric hydroxide (ii) negatively charged manganese dioxide and (iii) negatively charged antimony sulphide has been studied. In all these cases it has been found that sols get sensitised by the influence of the field.

176. The constitution of salts of cobalt in solution and their magnetic behaviour.

S. S. BHATNAGAR and A. N. KAPUR, Lahore.

Critical work on the magnetic properties of cobalt (from salts in various solvents) has been done and the theory of the change of the red solution of cobalt chloride to blue and *vice versa* is elucidated from magnetic properties.

177. A new magnetic balance and the magnetic susceptibilities of some allied diamagnetic compounds.

S. S. BHATNAGAR, K. N. MATHUR and T. K. LAHIRI, Lahore.

A new magnetic balance involving several new principles has been designed. The suspended system has been made very light and small. The beam has been shortened to about 3 cms. as compared to 20 cms. or more in the balances of Curie and Wilson type. The electromagnet employed carries specially shaped pole-pieces with a third pole-piece fixed in the middle. This arrangement gives two non-homogeneous fields in each of which a sample of the specimen is suspended. Equal weights of the specimen are taken and are contained in two similar thin glass tubes. The gradients of the non-homogeneous fields are arranged in opposite senses and a couple is thus exerted on the specimen when the electromagnet is excited. Observations are taken by a ballistic method, i.e., the electromagnet is excited for a definite short interval of time, with the same value of current each time and the corresponding "throws" of the beam are observed. This method very successfully overcomes the time and trouble involved in adjusting torsion heads to bring the specimen back to the initial position in the field. The balance has been used to determine magnetic susceptibilities of several closely allied diamagnetic compounds.

178. Investigations on the effect of crystalline structure on magnetic susceptibilities.

S. S. BHATNAGAR and R. N. MATHUR, Lahore.

In a paper communicated to Phil. Mag. in June last, a complete description of a new magnetic balance based upon the principle of interference of light has been given. Three allotropic forms of sulphur and the two isomeric modifications, red and yellow, of mercuric iodide were then investigated. A few changes, with a view to make the balance still more sensitive, have now been made in its construction and it has been used to determine the susceptibilities of the isomeric modifications of many other compounds, e.g., the red and yellow modifications of mercuric oxide. Many substances have been crystallised from different solvents when they come out with different crystalline structures and



their susceptibilities have been determined. As a result of this investigation, considerable light has been thrown on the mechanism of isomeric modifications.

### 179. Influence of light on the formation of some colloids.

MISS SHEILA ROY, Allahabad.

The hydrolysis of aqueous solutions of ferric chloride, ceric ammonium nitrate, chromic chloride, cobalt chloride and sulphate, nickel chloride and sulphate is markedly accelerated on exposure to light.

The measurements of electric conductivity, and pH values show that there are more hydrogen ions in the exposed solutions than those kept in the dark.

The extinction coefficient measurements show that the light absorption is more marked with the exposed solutions than the unexposed ones. This behaviour is possibly due to the formation of the hydroxides of the respective metals in the colloidal state.

It can be concluded from my experiments that the formation of colloids by the hydrolysis of salt solutions is facilitated on exposure to light. When, however, the solutions are exposed for a long time the colloids formed are precipitated. This behaviour is specially observable with solutions of ferric and ceric salts.

### 180. Influence of light on colloids.

MISS SHEILA ROY, Allahabad.

In continuation of my experiments on the influence of light on colloids I have carried on further work on Kohlschütter's silver sols, silicic acid sol obtained from the hydrolysis of silicon tetrachloride, uranium ferrocyanide, and hydrated manganese dioxide and cadmium sulphide sols.

My results show that uranium ferrocyanide, manganese dioxide and cadmium sulphide sols when fairly pure are readily coagulated by light. Although silver salts are highly photo-sensitive, Kohlschütter silver sol is not markedly sensitive to light and coagulates after a very long exposure. Silicic acid sol coagulates only partially on prolonged exposure to light.

Specially purified sols of chromium hydroxide, ceric hydroxide and zirconium hydroxide form jellies more readily in sunlight than in the dark.

An emulsion of fresh egg-white becomes unstable towards electrolytes on exposure to sunlight. On longer exposure the egg-white becomes yellowish coloured. An emulsion of egg-yellow becomes whitish yellow in sunlight and is partially coagulated.

### 181. Influence of $\text{OH}^-$ and $\text{H}^+$ ions on the viscosity of the sols of silicic, vanadic, and tungstic acids.

N. R. DHAR and S. GHOSH, Allahabad.

It has been observed with more than 30 sols that their viscosity in the presence of an electrolyte is intimately connected with the electric charge on the colloid particles. Our experimental results as well as those of other workers in this line show that other things being identical, the smaller the electrical charge on a colloid, the greater is its amount of hydration and hence the greater is its viscosity. Thus it has been observed with several positively charged sols like  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Zr}(\text{OH})_4$ , etc., that the viscosity goes on increasing and their stability towards their coagulation by electrolytes continuously diminishes as the process of dialysis is prolonged. The high viscosity of these unstable sols



markedly diminish as soon as traces of a stabilising agent like HCl, FeCl<sub>3</sub>, AlCl<sub>3</sub>, ZrOCl<sub>2</sub> etc., are added to the sols.

It has been noted that the sols of silicic, vanadic and tungstic are sensitized towards their coagulation in the presence of traces of an alkali, whilst smaller quantities of an acid make the sols stable. Larger quantities of an alkali render the sols stable and the greater amounts of an acid stabilise the sols. An explanation of this behaviour has been advanced, which assumes that the electrical charge of these negatively charged sols decreases on the addition of smaller quantities of an alkali and when larger amounts are added the electrical charge increases. On the other hand, traces of an acid increase the electrical charge on the colloids, whilst larger amounts decrease the electrical charge. Accordingly viscosity measurements were made with these sols with different quantities of H<sup>+</sup> and OH<sup>-</sup> ions. Our results show that (1) the addition of traces of an alkali increase the viscosity of the sols and when larger amounts are added the viscosity decreases, and (2) the smaller quantities of an acid decrease the viscosity of the sols, whilst in the presence of greater amounts the viscosity increases. These results, therefore, support our view that the greater the viscosity of a sol the less the electrical charge on the colloid advanced in 1925.

It may be of interest to note in this connection that Pauli and Valko (Koll. Zeit 38, 289, 1926) found that the cataphoretic movement of colloidal SiO<sub>2</sub> is far less in the presence of salts of weak acids than in the presence of KCl.

## 182. On the colloidal behaviour of the sols of silicic, vanadic, tungstic, molybdic, antimonie, and telluric acids.

S. GHOSH, Allahabad.

(1) Sols of silicic, vanadic, tungstic, antimonie, molybdic, and telluric acids contain a part of the substances in the molecular condition and a part in the colloidal state when freshly prepared.

(2) Molecular silicic, vanadic, molybdic, tungstic and antimonie acids gradually polymerise to bigger molecules with time and finally aggregate to form particles of colloidal dimensions. In the case of antimonie acid, this change is very rapid.

Thus molybdic acid, sol containing 1.550 grams of MoO<sub>3</sub> per litre when freshly prepared by the interaction of ammonium molybdate and hydrochloric acid, contains 47.8% of the substance in the molecular condition, which could pass through an ultrafilter. When kept for 120 hours at the room temperature the amount in the molecular condition decreases to 45.41%.

The viscosity of these sols increases, whilst the specific conductivity decreases when allowed to age.

(3) Telluric acid sol shows no change in the viscosity and specific conductivity with time.

(4) The sols of vanadic, silicic, tungstic, molybdic, and telluric acids are negatively charged. They are, however, sensitised towards their coagulation by electrolytes in the presence of small quantities of an alkali, whilst traces of an acid make the sols stable. Larger quantities of an alkali stabilise the sols and greater amounts of an acid render the sols unstable.

An explanation based on the existence of polymerised molecules in the sols has been advanced for this behaviour of the sols towards an acid and an alkali.



## 183. Adsorption by titanium dioxide sol.

L. S. BHATIA and S. GHOSH, Allahabad.

(1) A sol of titanium dioxide prepared by dropping  $\text{TiCl}_4$  slowly into water at  $18^\circ$  cannot be completely freed from  $\text{HCl}$  by dialysis. It was found that the sol containing 15.2 grams  $\text{TiO}_2$  per litre on prolonged dialysis gradually became more viscous and as soon as the pH value was less than 4.1 the whole mass coagulated as a gelatinous precipitate.

(2) The sol prepared at  $18^\circ$  adsorbed appreciable amounts of anions from different sodium or potassium salts and they are adsorbed in the following decreasing order:—

$\text{Fe}(\text{CN})_6''' > \text{NO}_2' > \text{SO}_4'' > \text{Cl}' > \text{S}_2\text{O}_3'' > \text{Cr}_2\text{O}_7'' > \text{Br}' > \text{Fe}(\text{CN})_6''' > \text{IO}_3' > \text{CrO}_4'' > \text{OH}'$ , the amounts of adsorption are expressed in moles per gram adsorbent.

The coagulating powers of different anions are in the following decreasing order:—

$\text{Fe}(\text{CN})_6''' > \text{Fe}(\text{CN})_6''' > \text{SO}_4'' > \text{Cr}_2\text{O}_7'' > \text{CrO}_4'' > \text{OH}' > \text{S}_2\text{O}_3'' > \text{IO}_3' > \text{NO}_2' > \text{Cl}' > \text{Br}'$ .

(3) The above results show that (a) the generally accepted view that an ion, which is highly adsorbed also possesses a high coagulating power is not supported by experiments, and (b) there is no justification that the greater the valency and hence the coagulating power of an ion the greater is its adsorption.

(4) The amount of adsorption of  $\text{OH}'$  ions by titanium dioxide sol is very small. The high coagulating power of  $\text{OH}'$  ions is due to the removal of the stabiliser  $\text{H}'$  ions by  $\text{OH}'$  ions.

(5) Titanium dioxide sol adsorbs more of an anion than a cation, with the liberation of  $\text{OH}'$  ions which increases the pH value of the sol (the pH value of the sol was 3.9). In no case, pH value was greater than 7.3.

(6) We are of opinion that titanium dioxide (also known as titanous acid) possesses more of basic character than acidic.

(7) A sol of titanium dioxide containing 15.2 grams of  $\text{TiO}_2$  per litre and prepared at  $18^\circ$  becomes stable towards its coagulation by electrolytes, shows a decrease in the specific conductivity and viscosity on ageing.

(8) On the other hand, a sol of titanium dioxide containing 10.2 grams of  $\text{TiO}_2$  per litre and prepared at  $55^\circ$  does not show any change in stability and the specific conductivity and viscosity increase very slightly on ageing.

(9) We are of opinion that a sol of titanium dioxide prepared in the cold becomes stable on keeping as free  $\text{HCl}$  present in the sol gradually acts on  $\text{TiO}_2$  forming  $\text{TiCl}_4$ , which gives out  $\text{Ti}^{++++}$  ions that are completely adsorbed by the sol and hence possess greater stabilising influence than  $\text{H}^+$  ions. This is not possible in the case of the sol prepared at  $55^\circ$ , as it is well known that chemical activity as well as the power of adsorption of a precipitate is considerably diminished when prepared in the hot condition.

## 184. Solubility of silver hydroxide and formation of silver sol at different temperatures.

RAI PARMATMA PRASAD MATHUR, Allahabad.

Careful experiments carried on with freshly prepared and purified silver hydroxide show that a saturated solution at  $31^\circ$  contain 0.0245 grm  $\text{Ag}$  per litre of solution. The solubility markedly increases with the rise in temperature.

The amount of Kohlschütter silver sol obtained by passing hydrogen



through saturated solutions of silver hydroxide at 50°, 60°, 70° and 80° has been determined. The amount of silver sol formed increases with the increase of temperature. Contrary to the observation of Kohlschütter it has been observed that the sol is quite stable at 70° and 80°.

185. On the critical potential of ferric hydroxide sol and the influence of its ionic environment on its rate of migration in an electric field.

J. N. MUKHERJEE and M. M. BISWAS, Calcutta.

The charges of ferric hydroxide sol at different dilutions at critical concentrations of electrolytes are being measured. The simultaneous determination of the transport numbers as also of electro-osmotic flow through pure ferric hydroxide precipitate are being carried out. The results are expected to reveal many points of interest. Also the influence of ionic environment on the rate of migration of the sol in an electric field is being studied.

186. Measurement of charge of arsenious sulphide sol in presence and absence of arsenious oxide and hydrogen sulphide.

J. N. MUKHERJEE and S. G. RAJKUMAR, Calcutta.

Further experiments on the stability of arsenious sulphide sol in presence and absence of arsenious oxide and hydrogen sulphide with different electrolytes have been carried out. Influence of constitution of the sol on such measurements have been pointed out from publications in this Laboratory (Mukherjee and Raichoudhuri and Bhattacharya, Journ. Ind. Chem. Soc., 5, 738, 1928). Also simultaneous measurements of transport numbers and electro-osmotic flow through pure  $\text{As}_2\text{S}_3$  are in progress.

187. The effect of dialysis and centrifugal action on the cataphoretic velocity of copper ferrocyanide hydrosol.

S. G. CHAUDHURY.

The hydrosols were prepared by precipitation of copper ferrocyanide, and subsequent peptisation with potassium ferrocyanide and then as dialysis was proceeded with, the cataphoretic velocity of the sol was measured from time to time. On dialysis, the cataphoretic velocity of a particular sample of sol showed increased value, though the sol became much more unstable. The current idea therefore, that the density of electrical charge decreases on dialysis thereby making the sol unstable is not correct. Subsequently it has also been shown that depending on the amount of precipitate peptised and the amount of ferrocyanide present, the cataphoretic velocity increases or remains constant. No decrease has been found up to the interval allowed for dialysis.

As a result of centrifugal action the cataphoretic velocity decreases, and the sol becomes unstable.

188. The effect of sugar on the cataphoretic velocity of copper ferrocyanide hydrosol.

S. G. CHAUDHURY and N. P. CHATTERJEE.

1. In presence of potassium chloride with or without sugar, the cataphoretic velocity at first decreases, then increases. There is another



decrease at high concentrations of potassium chloride, except in the case of 10% sugar, where the colloid coagulates.

2. In presence of sugar alone, the cataphoretic velocity at first decreases rapidly but the rate of variation of the velocity with higher percentage of sugar is small.

3. The rate of variation of the velocity with increasing concentrations of potassium chloride is smaller, the higher the percentage of sugar taken.

4. With barium chloride alone, the velocity continually decreases; in presence of 2.5% sugar, the same behaviour is observed though the initial drop is low and the final drop is high compared to the velocities observed in presence of barium chloride alone. *In the case of 5% and 10% sugar and with barium chloride we find an initial increase in the cataphoretic velocity at low concentrations of the electrolyte.*

### 189. The influence of the constituent ion on the stability of uranium ferrocyanide sol.

N. P. CHATTERJEE.

Uranium ferrocyanide sol in a high state of purity has been prepared. Its coagulation has been carried out in presence and absence of potassium ferrocyanide and uranium nitrate.

### 190. Liesegang rings in colloidal solutions.

R. N. MATHUR and K. G. MATHUR.

Formation of clear and well defined Liesegang rings has been observed by diffusing electrolytes into gels of agar-agar and gelatin impregnated with sols of  $\text{CdS}$ ,  $\text{Sb}_2\text{S}_3$ , and eosin. Completely dialysed sols and thoroughly washed gelatin and agar-agar have been used. The effect of the concentrations of the electrolyte and the sol on the formation of rings has been studied. The results are expected to throw light on the theories of Liesegang ring formation. Further work on the sols of Au, Ag and  $\text{Cu}(\text{OH})_2$  is in progress.

### 191. Stability of organo-sols.

N. A. YAJNIK and B. S. CHANDAR, Lahore.

In the present investigation an attempt has been made to study the conditions affecting the stability of organo-sols, such as zinc in acetone and copper in ethyl alcohol. It has been found that the stability of these systems is affected by the addition of electrolytes the same way as of the hydrosols. The order in which coagulation takes place by the addition of the electrolytes only is in accordance with the valency rule. The addition of non-electrolytes is found to bring about a sensitisation of the organo-sols towards the addition of electrolytes.

### 192. Effect of dilution of a colloid on electrolyte concentrations.

A. M. PATEL.

The effect of dilution of colloids on electrolyte concentrations has been recognised long ago. In a series of papers, Dhar, Ghosh and Sen have studied the changes in the concentrations of different sols when coagulated by different electrolytes. From the results, Dhar and Ghosh have formulated a general dilution rule which states that with the dilution of a colloid, the amount of an electrolyte required to coagulate the colloid becomes less and less provided that the sol does not appreciably



adsorb the ions carrying the same charge as the colloid from the precipitating electrolyte.

With a view to test the validity of the above generalisation, experiments on the coagulation of thorium hydroxide sol of—different concentrations and dialysed for different periods (*i.e.* containing different amounts of the peptising agent *viz.* HCl) were carried out.

From the results obtained, it is found that the dilution rule holds good in case of thorium hydroxide sol irrespective of the amount of the peptising agent present in the colloid. However, it is observed that with increase in the purity of the sol, the difference in the electrolyte concentrations required to coagulate the sol increases rapidly with dilution of the colloid. This is in accord with the fact that the dilution rule holds good only in those cases where the adsorption of the ions carrying the same charge as that on the colloid is negligible in comparison to the adsorption of the precipitating ions.

From the results, one is inclined to believe that the nature of the electrolyte as well as the relative adsorption of the stabilising and precipitating ions are mainly responsible for varying amounts of the electrolyte on the dilution of a colloid.

### 193. Effect of non-electrolytes containing different hydroxy groups on the peptisation of thorium hydroxide in presence of an excess of caustic soda,

G. M. NABAR and A. M. PATEL.

From the work on the peptisation of thorium hydroxide by non-electrolytes carried out by one of us (Patel) it was suggested that greater the number of the hydroxy groups present in a non-electrolyte, greater was its peptising power.

With a view to test the above suggestion the effect of non-electrolytes containing different numbers of hydroxy groups on the peptisation of thorium hydroxide was studied under different conditions.

It is found that greater amounts of non-electrolytes are required to peptise greater amounts of thorium hydroxide, when the amount of caustic soda and the volume of the system are kept constant.

It is observed that when the amount of thorium hydroxide and the total volume of the system are kept constant, less amounts of the non-electrolytes are required with increasing amounts of caustic soda.

When the amounts of thorium hydroxide and caustic soda are kept constant and the volume of the system is changed, it is found, that in cases of cane-sugar and glucose, the amounts required decrease while in those of ethylene glycol, glycerol, fructose and lactose, the amounts increase with the increase in the total volume of the system.

It is found that the peptising power of non-electrolytes increases with the increase in the number of their hydroxy groups. Fructose is, however, found to be an exception.

### 194. Adsorption of the chloride and the sulphate ions by thorium hydroxide sol in the absence and presence of non-electrolytes.

N. V. KAREKAR and A. M. PATEL.

It is a wellknown fact that adsorption, besides some other factors, is mainly responsible for the coagulation of colloids by electrolytes. The effect of non-electrolytes on their stability is also attributed to their adsorption by the colloids.

Experiments were carried out to study the adsorption of the chlorides of the alkali metals and the sulphates of the mono-, bi- and tri-valent



metals in the absence and presence of some non-electrolytes (*viz.* methyl, ethyl and propyl alcohols) by thorium hydroxide sol with decreasing amounts of the peptising agents, *i.e.*, with progress of dialysis.

It is found that the non-electrolytes cut off the adsorption of all the chlorides in all cases and of the sulphate ions of the mono and bi-valent metals while the adsorption of the sulphates of the trivalent metals is increased in the presence of non-electrolytes. The order of their adsorption was not the same as that of their coagulating power showing, therefore, that it is wrong to assume that coagulation and adsorption go hand-in-hand. From the results, it can, at once, be seen that the systematic study of the adsorption of the electrolytes by colloids (and not by the precipitated substances) is bound to shed a flood of light on the mechanism of coagulation.

195. Kinetics of the coagulation of arsenious sulphide sol.  
SHRIDHAR SARVOTTAM JOSHI *and* RAMESH S. M. PRABHU,  
Benares.

The paper contains a critique of the various existing methods of measuring the coagulation velocity of the colloids. In this work the percentage coagulation produced in a finite time has been determined directly by an analysis of the coagulum at different temperatures, and with varying initial concentrations of the colloid. Regular curves are observed relating the colloid concentration with time, at successive stages during coagulation, and the corresponding viscosity of the system. The results are discussed in the light of Smoluchowski's equation.

196. Coagulation of manganese dioxide sol. Part I. The influence of temperature, and of the colloid and electrolyte concentration.

SHRIDHAR SARVOTTAM JOSHI *and* T. S. NARAYAN, Benares.

Results are given for the coagulation of the above sol over a wide range of temperature and of the concentrations of the precipitating electrolytes, as well as of the colloid material, the last containing a very small quantity of KOH. Interesting results are observed regarding the temperature effect. The coagulation rate diminishes continuously with temperature till about 30°C, and then increases as the temperature is increased. A departure from the Smoluchowski's equation is observed in the results for the influence of the concentration of the coagulating electrolyte.

197. The coagulation of the manganese dioxide sol. Part II: The behaviour of the electrolyte free sol.

SHRIDHAR SARVOTTAM JOSHI *and* T. S. NARAYAN, Benares.

The manganese dioxide sol prepared in the familiar J. Cuy's method contains a small amount of KOH. Attempts at removing this by dialysis result in the instabilisation of the colloid, except when the process is carried out at temperatures well above 60°C. A new method which gives an electrolyte free sol has been developed. It is to carry out the dialysis with a negative potential applied to the dialysing septum. The stability period of the resultant sol has been observed to increase as the magnitude of the applied potential is increased. This sol is also found to be markedly sensitive towards electrolytes, as well as to any solid heterogenities that might be introduced in the system.



## 198. Studies on the effect of ultraviolet light on colloids, Part II.

PANNA LAL and P. B. GANGULY, Patna.

In a previous paper (*Jour. Ind. Chem. Soc.*, 1929, 6, 547) the coagulation of a number of colloidal solutions by ultraviolet light has been studied. A further series of colloids have been prepared in which the usual charge on the particles has been reversed, and exposed to ultraviolet light. It has been found that both positively as well as negatively charged colloids are coagulated equally well by light. These results do not support the conclusion of Crowther (*Phil. Mag.*, 1927, 4, 325; *ibid.*, 1929, 7, 86) that the coagulating action of radiations is restricted to negatively charged colloids only.

## 199. Studies on the effect of ultraviolet light on colloids.—Part III.

P. C. SINHA and P. B. GANGULY, Patna.

A series of peptised colloidal solutions have been prepared by using sodium soaps, sodium lysalbate, sodium protalbate, and gelatine as the stabilising agents and exposed to the action of ultraviolet light. Coagulation occurred in a majority of cases. Solutions of the peptising agents themselves were also exposed individually to ultraviolet light. Measurements of PH values, conductivities, and in certain cases viscosities, of the exposed and the unexposed solutions indicate considerable chemical changes, showing that the coagulation of the peptised colloids is primarily due to the chemical decomposition of the peptising agents by light.

## 200. The emulsifying action of colloidal sulphur.

BASRUR SANJIVA RAO, Bangalore.

When a very dilute solution of iodine or bromine in benzene is shaken with an excess of an aqueous solution of hydrogen sulphide the benzene layer becomes turbid. The turbid liquid clears on treatment with dehydrating agents but regains its turbidity on shaking with water.

As a result of systematic investigation it has been concluded that the turbidity is due to an emulsion of water in benzene the emulsifying agent being a colloidal form of sulphur, which is hydrophilic and at the same time stabilised in benzene by persulphides of hydrogen.

## 201. On 'activated' charcoal.

S. P. RAICHOUDHURI, Calcutta.

1. The adsorption of inorganic acids by charcoal has been found to be purely molecular.

2. Adsorption of electrolytes by various kinds of activated charcoal has been carried out. The results have been discussed from the point of view of current theories of adsorption.

3. Effect of heating the charcoal at different conditions has been studied. It is found that the charcoal is most active when heated in an atmosphere of pure nitrogen.

4. The so-called negative adsorption by charcoal has been found to be due to removal of water by charcoal.

5. Very pure form of animal charcoal has been found to be positively charged which on the addition of very small concentrations of hydrochloric acid becomes negatively charged.



## 202. Preparation of some hydroxide and other inorganic jellies.

SATYA PRAKASH and N. R. DHAR, Allahabad.

1. The conditions of the formation of various new jellies have been investigated.

2. We have prepared hydroxide jellies of iron, chromium, aluminium, tin and zirconium by the addition of sodium acetate to chlorides or nitrates of these metals; wherever it was found necessary, various amounts of ammonium sulphate and ammonia have also been added but all these jellies have been obtained in acid medium. It has been shown that for the preparation of zirconium and ferric hydroxide jellies, no addition of ammonia is necessary while in the case of chromium and tin, large quantities of ammonia have to be added before obtaining a jelly. In the case of aluminium, only a small amount of ammonia yields a jelly. The nature of these jellies has also been studied.

3. We have also obtained new jellies of chromic tungstate, zirconium molybdate, zirconium borate, ceric arsenate and ceric borate by dialysing the mixtures of chromic chloride, zirconium nitrate, and ceric ammonium nitrate with sodium tungstate, potassium molybdate, potassium arsenate and borax solutions, and coagulating the sols thus obtained by various electrolytes.

## 203. Soap gels in alcohol.

S. N. BANERJI and S. GHOSH, Allahabad.

Soap gels of different concentrations were prepared in alcohol with sodium palmitate and the phenomenon of hysteresis in the sol-gel transformation was studied. It was found that as the concentration of the gels increased the degree of hysteresis passed through a minimum. The process of gelation resembles the crystallisation from a supercooled solution. Thus the setting of sodium palmitate gels in alcohol is remarkably favoured by shaking and by inoculating the sol with already formed gels. Similar results were obtained by Hardy (Proc. Roy. Soc. 87, 29, 1912) with azomethine gels and Baratte (compare Hardy loc. cit.) with gelatin gels. Our results with sodium palmitate gels of different concentrations on the phenomenon of hysteresis on the sol-gel transformation can be easily explained on this view.

It may be of interest to note that several years ago Tammann (Z. Physik. Chem. 25, 441, 1898) observed that at very low temperatures that substances like molten phosphorus, azobenzene, benzophenol, etc., lose all capacity of crystallisation and maintain their glassy character. These results are also in support of our view advanced with soap gels.

## 204. The influence of the concentration of coagulating electrolytes, time and temperature on the syneresis of some inorganic jellies.

SATYA PRAKASH, Allahabad.

1. The phenomenon of syneresis of the following jellies has been studied from various view points:

Ponceaux-red, ferric phosphate, ferric arsenate, chromium arsenate, vanadium pentoxide, zirconium hydroxide, zirconium molybdate, zirconium borate, ferric borate, and manganese dioxide.

2. It has been observed that greater the concentration of the coagulating electrolyte, the greater is the amount of syneresis, and this has been explained on the basis of the influence of electrolytes on hydra



tion and agglomeration tendency of particles forming the net-work of the jelly.

3. It has been observed that the syneresis starts a short time after the setting of the jelly and the amount of syneresis increases with time up to a limiting value but after this limit the rate of increase diminishes.

4. The influence of temperature on the syneresis of these jellies has also been investigated. It has been observed that the amount of syneresis is markedly increased at higher temperatures. Experiments have been carried on at three temperatures,  $30^{\circ}$ ,  $50^{\circ}$  and  $70^{\circ}\text{C}$  and it has been found that the temperature coefficient between  $30^{\circ}$  and  $50^{\circ}$  is much less than that between  $50^{\circ}$  and  $70^{\circ}$ .

5. In many jellies, such as those of iron, chromium and aluminium hydroxides and arsenates, phosphates and molybdates of thorium, only very little syneresis has been observed when kept for months but the jellies of stannic hydroxide, borate and tungstate synerise readily.

## 205. On the development of acidity in soils.

**J. N. MUKHERJEE and H. K. SEN, Calcutta.**

The nature of electrometric titration curves of sparingly soluble acids such as cinnamic acid, as also silicic acid gel and aluminium hydroxide sol are being studied. The temperature co-efficient of acid liberation by hydrated and dehydrated silica in contact with different electrolytes has been investigated and the results discussed from the theoretical standpoint.

## 206 The optimum conditions for the formation of silica gel from alkali silicate solutions. Part II.

**R. C. RAY and P. B. GANGULY, Patna.**

In a previous paper (reported to the Science Congress last year), the optimum conditions for the formation of silica gel from alkali silicate solutions, where the ratios of the alkali oxide to silicon dioxide were as 1:1 and 1:2, were studied. The present paper describes further extension of the work, and the conditions of gel formation have been examined in the case of sodium silicate solutions containing higher ratios of silicon dioxide, the highest being the case where the ratio  $\text{Na}_2\text{O}/\text{SiO}_2$  is equal to 4.

The gel formation by the action of ferric chloride on sodium silicate solutions has been further investigated by measurements of heats of reactions.

## 207. Adsorption of ions by hydrated silica, alumina, and aluminium silicates.

**A. NAGARAJA RAO, Bangalore.**

The ionisation of amino-acids giving rise to restricted quantities of both OH and H ions has been known to be the cause for the maintenance of a fairly uniform pH value in body fluids. The complex alumino-silicates seem to be responsible for a similar adjustment of pH values in soil. Experiments are in progress to explain from the point of view of adsorption the complete role played by these complex alumino-silicates in maintaining the pH value in soils.

## 208. Adsorption of alkali sulphites by silicic acid gel.

**SARJU PRASAD, Benares.**

Results are given for the adsorption of sodium sulphite from its solution on the gel which was prepared according to the method elabora-



ted by Patrick and Megarack (Journ. Amer. Chem. Soc. 1920, 212, 946) in an atmosphere of nitrogen. The temperature was varied over a wide range, and the influence of an initial addition of sodium sulphate was studied. The results are found to be in good agreement with the Freundlich's equation for the adsorption isotherm.

209. Condition of sparingly soluble substances when formed in presence of a gel: Lead iodide in agar-agar and gelatine.

M. D. PANDAY and A. C. CHATTERJI.

In a recent paper (Trans. Faraday Soc., 1928. 24. 461.) Bolam and Mackenzie came to the conclusion that  $\text{PbI}_2$  in agar-agar remains in a supersaturated condition. It has been emphasised and shown experimentally in a number of previous papers (Jour. Ind. Chem. Soc., 1928. 5. 175; Trans. Faraday Soc., 1926 72. 23; Koll. Zeit., 1926. 40. 97; 1925. 35. 2, 89) that sparingly soluble substances when formed in presence of a gel exist mainly in the colloidal state. Bolam and Mackenzie's results have been scrutinised and it has been shown that from their own experimental results it is difficult to accept their conclusions.

In this paper the electric conductivity of  $\text{PbI}_2$  in agar-agar and ash-free gelatine has been measured. Agar-agar was well washed first with distilled water and finally with conductivity water till the conductivity of the supernatant liquid did not increase. Agar-agar was tested to be free from sulphate ions.

The results obtained are in complete harmony with our former views. In fact, the conductivity of lead iodide in agar-agar is less than the conductivity of  $\text{PbI}_2$  of an equal concentration when freshly precipitated in conductivity water, proving thereby that lead iodide is more soluble in water than in an agar-agar sol.

210. Ignition points of the electrolytic mixture ( $2\text{H}_2 + \text{O}_2$ ) and ( $\text{H}_2 + \text{O}_2$ ).

H. K. SEN and SUKHAMOY CHATTERJEE, Calcutta.

Since the publication of a paper by one of us and H. N. Chatterjee (J. Indian Chemical Society, 1929) on the ignition temperature of some inflammable gases, the rather unexpected lower ignition point of the electrolytic gas mixture has led us to investigate more accurately this point. As the reading of very small current differences by ammeters might vitiate the results and inference, we used the potentiometric method for accurately finding the current strengths. The following results were obtained with soap bubbles of 50 c.c. capacity:—

Composition of gases.	Bridge reading.	Current in ampere.	Difference.
Hydrogen : Oxygen 2 vols. : 1 vol. 1 vol. : 1 vol.	22.7 cm. 23.2 cm.	3.36414 3.43824	} 0.0741



## 211. Esterification in mixed solvents.

B. V. BHIDE.

Esterification of phenyl-acetic acid in amyl alcohol-benzene mixtures at constant acid-catalyst concentration has been studied at 30°C. with hydrogen chloride as catalyst. The velocity coefficient-composition curve shows a well marked minimum at 50% benzene concentration. With 90% benzene, the coefficients are higher than in pure alcohol. Surface-tension curves of mixtures of benzene and amyl alcohol show no discontinuity.

212. Physical properties of acetates in anhydrous acetic acid.  
Part I.

B. V. BHIDE.

Viscosities and densities of solutions of Li, Na, K,  $\text{NH}_4$ , Co, Hg, Pb, Ba, and Mg have been determined. At 0.5N concentration the viscosity increment follows the order  $\text{Ba} < \text{K} < \text{Mg} < \text{Pb} < \text{Na} < \text{Li}$ . The viscosity increment increases with increasing atomic weight more rapidly than metals of low atomic weight. Acetates of Ca, Cd, and Mn are insoluble in acetic acid. Mercury and cobalt acetates are sparingly soluble. Further work is in progress.

## 213. On Rhythmic Structures.

P. B. GANGULY and D. N. GHOSE, Patna.

Rhythmic structures in capillary spaces in the absence of a gel have been obtained by Notboom (*Kolloid-Z.*, 1923, 32, 247), Brodersen (*Kolloid-Z.*, 1924, 35, 21), and others. Further experiments have been performed on a large series of reacting pairs of solutions, and it is found that the phenomenon is a general one with nearly all precipitates, crystalline or colloidal. These structures are obtained when two drops of the reagents, separated by a paraffin line on a clean glass plate, are covered by another similar plate, and the two advancing surfaces are just caused to meet by slight movement of the top plate. In most cases, although the reaction is continuous the final structure is found to be periodic. The cause of formation of these structures has been discussed in the light of some of the theories advanced to explain the well-known Liesegang phenomenon.

## 214. Importance of the oceanic salt deposits to geologists.

S. K. RAY, Dhanbad.

In 1861 Bunsen first of all suggested that the etherial magmas are comparable to complex solutions of salts in water. In the ocean the geologists have one such complex solution.

Döltler's experiments (1907-1908) have conclusively proved that the magma conducts electricity and dissociation of the silicate melts (solution) takes place exactly in a manner similar to the ionised solution of salts.

Very important light has been thrown on the constituents of the magmas and on the types of molecular equilibria present therein by the practical application of Gibbs's Phase Rule (1874) on the magmatic solution by Niggli, Bowen, etc. Accord. to Niggli the principal components of magma are Kp, Ne, Ts, Gl,  $\text{N}_s$ ,  $\text{K}_s$ , Co, Fa, Fo, Q, W, O, Mt. and Sp. Molecular equilibria, as are represented by different phases, originate through polymerisation, formation of double salts, addition (silicification), subtraction (entsilicification), etc., of those components. Elements contained in these components take certain characteristic positions in the periodic curve.

Just in a similar manner, the sea water too contains components, chlorides, sulphates, etc., which, on the drying up of the ocean basin,



separate into various mineral phases due to reactions similar to what have been enumerated in case of the magma. Moreover, there seems to exist certain definite mathematical relation between the ionic number of the principal elements of the sea salts.

215. The densities, compressibilities and dielectric coefficients of silanes.

G. GUNDU RAO, K. L. RAMASWAMY and H. E. WATSON,  
Bangalore.

Mono- and di-silanes have been prepared by the action of hydrochloric acid on magnesium silicide and their separation and purification have been effected by fractional distillation. Values for the densities have been obtained at room and solid CO<sub>2</sub> temperatures. Approximate values of the compressibilities have also been determined in order to evaluate the electric moment from the values of the dielectric coefficients. An apparatus permitting the simultaneous determination of density and compressibility at different temperatures has been employed. The dielectric coefficients of the two gases have been measured by the heterodyne method at high frequency at different temperatures.

216. Alcoholysis in Mixed Solvents.

Z. H. PATEL, Bangalore.

The action of methyl and ethyl alcohols on the esters of propionic and butyric acids has been studied dilatometrically at two temperatures in the presence of benzene using hydrochloric acid as a catalyst. The mean temperature coefficient between 30° and 40° is 1.84.

The velocity coefficients reduced to the same quantity of alcohol increase with the amount of benzene. Reactions with 99 per cent. alcohol-benzene mixtures have also been conducted.

Experiments tried with different concentrations of the catalyst show the velocity coefficients to be proportional to the concentration of the catalyst even in presence of fifty per cent. of benzene. It is shown from conductivity data that the hydrogen ion is not the only catalytic agent but that the undissociated molecule also acts as a catalyst.

It is suggested that a change in the degree of association of the alcohol on addition of benzene may be a factor in changing the velocity coefficient.

217. The solidification points of capric and stearic acids and their mixtures.

Z. H. PATEL, Bangalore.

The freezing points of a complete range of mixtures of capric and stearic acids have been determined. The curve obtained by plotting percentage composition of the acids against freezing points does not show any breaks, indicating thereby no tendency to compound formation. The eutectic mixture which melts at 26.65° contains 90 per cent. of capric acid.

218. The conductivity of soaps in alcoholic solutions.

B. S. V. K. VITTAL.

The sodium and potassium soaps of pure oleic and stearic acids have been prepared and the conductivities of their solutions in aqueous alcohol



of varying concentrations ranging from 0—100 per cent. of alcohol determined.

Viscosity measurements of the solutions have also been made and the curves connecting molecular conductivity with dilution studied.

219. The heats of transition of triglycerides.

M. M. RAMA RAO and S. K. KULKARNI JATKAR.

A method has been developed for measuring latent heats of fusion by means of a twin calorimeter to which heat is supplied at a known steady rate, the time for fusion being determined. This has been used for measuring the heats of fusion of the two forms of tristearin, the difference corresponding with the heat of transition.

A method also employing a double calorimeter has been applied to the determination of the heats of solution of the two modifications of tripalmitin and tristearin in several organic solvents. The difference in the heats of solution of the two forms is constant and equal to the difference in the latent heats, indicating that in solution these bodies assume the same form.

220. Adsorption isotherms in non-aqueous systems.

J. G. KANE.

A study of the system toluene-acetic acid with respect to its adsorption isotherm has been made for three adsorbents, activated silica and animal and sugar charcoals. The results obtained indicate that the preferential adsorption of either of the components depends on the nature of the adsorbent and its activity. With animal charcoal, toluene is preferentially adsorbed at low toluene concentrations and acetic acid at toluene concentrations above 60 per cent.

With sugar charcoal toluene is preferentially adsorbed at all concentrations and with silica the reverse phenomenon is observed.

221. The systems sulphuric acid—methyl ether—propyl ether.

N. G. GAJENDRAGAD.

Pure sulphuric acid was mixed with methyl and propyl ethers and the electrical conductivity, viscosity, surface tension and density of the mixtures were measured in a specially designed cell. The data are discussed from the point of view of intermediate compound formation.

222. Fusibility of mixtures of sodium carbonate with calcium carbonate and with lime.

R. C RAY and V. DAYAL, Patna.

Mixtures of carbonates of sodium and calcium fuse by rapidly heating them at temperatures below 700°. The maximum fusibility is obtained with mixtures containing 5–6% of calcium carbonate. The fusibility of sodium carbonate and calcium carbonate mixtures is found to be greater than sodium carbonate and lime mixtures. The fusion of sodium carbonate and calcium carbonate mixture is accompanied by partial decomposition of the calcium carbonate, especially in an atmosphere free from carbon dioxide. By prolonged heating practically the whole of carbon dioxide is lost by the calcium carbonate, and the fusibility of the resulting mixture is considerably diminished.



223. The systems,  $\text{KMnO}_4\text{—KBF}_4\text{—H}_2\text{O}$  and  $\text{KClO}_4\text{—KBF}_4\text{—H}_2\text{O}$ .

R. C. RAY and K. K. CHATTERJI, Patna.

Zambonini (*Z. Kryst. Min.*, 1905, **41**, 60) and Barker (*Jour. Chem. Soc.*, 1912, **101**, 2484) have stated that potassium fluoborate and perchlorate are isomorphous. Zambonini (*Atti. R. Accad. Lincei.*, 1922, [V], **31**, ii, 67) has also found a slight miscibility, up to 0.4 per cent. of potassium permanganate with the fluoborate but on the permanganate side the miscibility was found to be practically zero. We have found, however, that when either a crystal of potassium chlorate or a crystal of potassium permanganate is suspended in a saturated solution of potassium fluoborate overgrowth crystals are formed in both cases. In order to determine whether mixed crystals (solid solutions) of limited composition only or double salts are formed, a phase-rule study of the above-mentioned systems has been made.

224. The Ternary System  $\text{K}_2\text{SO}_4\text{—CdSO}_4\text{—H}_2\text{O}$  at  $25^\circ\text{C}$ .

K. L. MALHOTRA, H. D. SURI and A. R. SHARMA.

(1) The usual Schreinemakers diagram (at  $25^\circ\text{C}$ ) shows an increase in the solubility of  $\text{K}_2\text{SO}_4$  on the addition of  $\text{CdSO}_4$  up to the triple point.

This indicates the formation of the double salt in solution over a considerable range.

(2) The solubility curve at  $25^\circ\text{C}$  indicates a small increase in the solubility of  $\text{CdSO}_4$  on the addition of increasing amounts of  $\text{K}_2\text{SO}_4$ . This is not traceable in the triangular diagram.

(3) The addition of  $\text{K}_2\text{SO}_4$  to a saturated solution of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  causes the separation of an anhydrous double salt,  $\text{CdSO}_4, \text{K}_2\text{SO}_4$ .

225. The System  $(\text{NH}_4)_2\text{SO}_4\text{—CdSO}_4\text{—H}_2\text{O}$  at  $25^\circ\text{C}$ .

K. L. MALHOTRA and H. D. SURI.

(1) The solubility of  $(\text{NH}_4)_2\text{SO}_4$  is decreased by the addition of  $\text{CdSO}_4$ , while the solubility of  $\text{CdSO}_4$  is increased by the addition of the other component.

(2) The conjugation lines intersect within the triangle representing the ternary system, confirming the separation of the stable double salt  $(\text{NH}_4)_2\text{SO}_4, \text{CdSO}_4, 6\text{H}_2\text{O}$ , c.f.  $\text{MnSO}_4, \text{Na}_2\text{SO}_4, 2\text{H}_2\text{O}$  reported by Caven and Johnston (*J. Ch. Soc.* 1928, 2506).

(3) The solubility curve at  $25^\circ\text{C}$  shows the existence of this stable double salt when the solution contains from 0.13 to 3.63 molecules of  $\text{CdSO}_4$  per molecule of  $(\text{NH}_4)_2\text{SO}_4$ .

226. Further experiments with the calomel electrode.

K. K. KUMAR, Calcutta.

Experiments with the calomel electrode and hydrochloric acid and potassium chloride at very low concentration have been continued.

227. Reduction of aromatic nitro-compounds with sugar.

TARINI CHARAN CHAUDHURI, Pabna.

Among other reduction products isomeric azo-benzenes have been obtained.







# INDIAN SCIENCE CONGRESS.

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ABSTRACTS OF PAPERS.

Section of Agriculture.

*President :—Diwan Bahadur Sir T. Vijayaraghavacharya,  
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## Section of Agriculture.

### *Abstracts.*

#### SOIL SCIENCE.

1. Soil conditions as affecting the growth and maturity of sugarcane in the district of Saran in North Bihar.

M. N. GHOSH, Sabour.

Saran is an important cane-growing district and its situation between two big Himalayan rivers is described. When the rivers are in high flood, the subsoil water-level in the tracts bordering on them, rises very high. In consequence with an early cessation of the rains in any year or even a long break in the rains conditions arise in the soil leading to a rise of salts. The cane C0213 is one of the first to succumb under these adverse conditions. The leaves turn yellow, the growth of the cane stops, and carbohydrate formation remains at a stand-still. If the cane revives, on the conditions becoming favourable again, it does not ripen properly, but yields a juice of very low richness at the time when it ought to be ripe. C0210 and C0205 are more tolerant of such soil conditions and are not as visibly affected as C0213, but even they do not show a sharp maturity and do not yield juice of high sugar content.

The concentration of salts at various depths between the months February and August and the condition of the cane as affected thereby, are described. From the composition and the proportion of the water-soluble constituents of the soil, it appears that a decrease of lime and an increase of soda salts together with a comparatively dry condition of the soil, occurs just when the canes begin to get 'sick'. Treatment of the soil with calcium cyanamide in July is suggested.

2. Relation between the fluctuations in the subsoil water-table and the nature of crops reared.

N. K. BOSE.

A statistical examination of this problem has been made in an area commanded by a canal in the Punjab. In this case the amount of water from irrigation put on the soil has been correlated with the fluctuations in the subsoil watertable. This has been done in the case of 3 different crops and shows the relative importance of these crops in affecting the watertable.

3. Determination of the frequency curves of soil samples by measuring the variations of hydrostatic pressure.

R. C. HOON and N. K. BOSE.

By the Odeen-Keen balance frequency curves of soil samples are worked out from the accumulation curve. In this experiment the pressure curve is obtained photographically after dropping a small quantity of soil in a tall cylinder full of water. The waterlevel in a small pressure tube connected with the tall cylinder at a depth 'h' below the water surface rises as soon as the soil sample is poured in and remains at this highest point till the first soil particle passes the mouth of the pressure pipe; after this there is a continuous fall in the water meniscus



till a steady level is reached. The difference between this level and the initial level being the rise in the meniscus due to a displacement of water in the tube by the soil sample, affords a very accurate measure for the total volume of soil used. From this pressure curve the frequency curve is derived from the following relation :—

$$F(\gamma) = -\frac{+2}{\gamma} \frac{d^2p}{dt^2}$$

where  $F(\gamma)$  is the distribution curve

and 
$$P = \frac{p(o) - p(t)}{p(o) - p(s)}$$

in which  $p(o)$ ,  $p(t)$  and  $p(s)$  correspond to the ordinate of the pressure curve at time  $o$ ,  $t$  and  $s$ .

A number of soil samples has been treated by this method and gives very good results.

#### 4. Nitrogen fixation in the 'kalar' or salt lands of Sind.

V. A. TAMHANE and P. G. KRISHNA, Sakrand (Sind).

The alluvial soils of Sind abound in 'Kalar' or soluble injurious salts. They generally contain only a small quantity of organic matter and their nitrogen contents are low. Yet, it was found that the nitrogen contents were not materially reduced although crops were being taken from the land year after year. It was therefore thought necessary to study the nitrogen fixation in the kalar or salt lands as compared to good land in Sind. As the soils also contain a large quantity of lime it was thought desirable to see the effect of different calcium salts and of calcium oxide on the nitrogen fixing organisms.

It was found that even a small quantity of sodium carbonate (0.02%) considerably inactivated the nitrogen-fixing organisms, while appreciably large quantities of the total soluble salts (1.5%) consisting mostly of sodium chloride and sodium sulphate only rendered these organisms slightly inactive. Of the calcium salts used calcium chloride and calcium sulphate were found to stimulate nitrogen fixation. The oxide of calcium, however, was found to depress the process of nitrogen fixation.

#### 5. The intensive use of fertilisers and its effect on the composition of the soil clay.

B. VISWA NATH, S. KASINATHAN, and G. K. CHIDAMBARAM, Coimbatore.

The influence of intensive manuring with artificials on the exchangeable bases of soils are studied.

These influences are confined only to the surface layer of the soil.

Agreement with Page and Williams is obtained when these manures are arranged in the order of their lime-replacing powers except in the case of ammonium sulphate.

An alternative theory of the action of ammonium sulphate is put forward and evidence in support of the same is advanced.

#### 6. On the origin and nature of tropical peat.

T. R. N. PILLAY and V. SUBRAHMANYAN, Bangalore.

A systematic study of the chemical nature and the mode of distribution of organic matter in the *Kari* soils of Travancore as related to the past and the present vegetation has been made. The chemical changes and the biological transformations resulting in the accumulation of (a)



wood resins and tar, (b) soluble iron and aluminium salts, and (c) certain labile sulphur compounds have been studied.

7. On clay as an acid.

JNANENDRANATH MUKHERJEE, Calcutta.

The paper contains a review of the theories put forth to account for the acid properties of clay, specially in relation to soil acidity and base exchange. The experiments of H. K. Sen in the writer's laboratory are discussed in the light of these theories. Further experiments are in progress.

**ELECTRICITY IN AGRICULTURE.**

8. The application of electro-cultural methods to the treatment of certain plant pests and diseases.

S. S. NEHRU, Naini Tal.

Plants affected with rusts and smuts and aphids and leafcurl have been subjected to electro-cultural treatment and varying measure of success in eliminating the pest or disease concerned, registered. The plants treated were wheats, barleys, mustard, and chillies.

9. The application of electro-culture to the cultivation of the cotton plant.

S. S. NEHRU, Naini Tal.

The results of cotton cultivation in the plains as well as in the hills with the application of different comparative methods of electrocultural treatment are described.

10. The application of electro-culture to the cultivation of the sugarcane plant.

S. S. NEHRU, Naini Tal.

The results of the cultivation of sugarcane cuttings as well as ratoons in poor and bad soils and the application of electro-cultural treatment with a view to hardening the plant against the white ant pest in the former and saline efflorescence in the latter are described.

11. The application of electro-culture to the cultivation of the potato plant.

S. S. NEHRU, Naini Tal.

The results of the comparative tests of efficacy of different modes of electro-cultural treatment of the potato plant in the plains as also the results of electro-cultural experiments with different varieties of potatoes with varying resting periods during potato cultivation in the hills are described.

12. The application of electro-culture to the germination of the teak seed.

S. S. NEHRU, Naini Tal.

The results of applying electro-cultural methods to the germination of the teak seed in the plains as well as the hills are described.



13. The application of electroculture to the germination of the Cinchona seed.

S. S. NEHRU, Naini Tal.

The results of applying electro-cultural methods to the germination of the cinchona seed are described.

14. The application of X-rays to the germination of certain seed varieties.

S. S. NEHRU, Naini Tal.

The results of applying different dosages of X-rays to germination of teak, cotton, and cauliflower seed are described.

15. Electricity and farming.

C. MAYA DAS, Cawnpore.

The attention of many countries including some Provincial Governments in India is engaged on the subject of rural electrification. The main reasons for this are (1) cheapness of power, (2) ease of operation. Experiments at the Agricultural College, Cawnpore, have shown that for thrashing of wheat and chopping of fodder electric power is considerably cheaper than that supplied by a petrol paraffin engine. For the thrashing of wheat this is so even when electric current sells at 2 annas 6 pies per unit. The U. P. Government have a Hydro-Electric Scheme by which electrical power will be available at 1 anna per unit. At this rate, certain farm operations can be performed very economically. Incidental references are made to the cost of such operations by the older country methods which work out at a considerable disadvantage with reference to cost.

16. Studies on quality in crops. I. Electrical treatment as a means of improving the quality of malt.

K. VENKATAGIRI, V. SUBRAHMANYAN, and T. J. MIRCHANDANI, Bangalore.

High prices are being paid by brewers for malts which contain low percentages of nitrogen and give extracts of high gravity.

It has been found that by passing an alternating current (25 cycles, 210 V., 0.1—0.15 amp.) for about 1 hour through a weak salt solution (sodium nitrate, 1%) in which barley (Plumage Archer) is packed between carbon electrodes, a malt possessing the desired qualities can be obtained. Thus, the nitrogen content decreases from 0.22% in the malt prepared from untreated barley to 0.14% in that from the same barley after electrical treatment. The gravity of the wort rises from about 1040 as obtained from the former to about 1605 as obtained from the latter.

The industrial possibilities of the foregoing and the related observations are discussed.

### **FERTILISERS.**

17. A new synthetic manure from sewage, town refuse, and waste vegetation.

J. JAGANNATHA RAO and V. SUBRAHMANYAN, Bangalore

By spraying sewage on refuse and waste vegetation previously treated with minute quantities of insecticides and fungicides like cupric hydroxide, or bleaching powder under fully aerobic conditions, it has been possible to obtain in under two months a compost suitable for immediate application to land. The decomposition is hastened and the manurial value in-



creased by previous addition of lime, nitrogen, and phosphate to the refuse. Previous treatment of the sewage is unnecessary as the same type of results have been obtained by treating with activated sludge and raw sewage in equivalent proportions. The decomposition is however slow and offensive odours develop only when previous spraying with the insecticides and fungicides is omitted. Copper has been found to be the cheapest and most effective of the elements so far tried, no more than 20 gms. as commercial copper sulphate being required to treat 1 ton of refuse or waste. The synthetic manure, which can be made without addition of any nitrogen as starter, is very much richer than farm-yard manure and can be marketed profitably at less than one rupee a ton. Trials have also shown that (a) the copper which passes into the soil as the carbonate has no deleterious action on crops, and (b) the process can be extended to develop a new, economic, and hygienic system of sewage disposal.

#### 18. The preparation of manure from plantain stems.

V. N. GOKHALE, Poona.

Among the fruit trees, plantains occupy a high position as regards cultivation in the Bombay Presidency. Plantain stems do not decompose either easily or within a short time and this constitutes a difficulty in their use for industrial purposes, such as fibre-making or paper-making; it is also difficult to turn them to manure. Experiments to transform them into a suitable manure in a short time were tried. The stems were chopped into small pieces and treated under different conditions such as putting them in pits, in heaps, and in trenches with either lime or calcium cyanamide or with both. The best results were obtained when the stems were treated with both lime and calcium cyanamide. The manure was ready within six months time, with a gain of nitrogen from 0.4 per cent to 1.18 per cent.

#### 19. Manurial value of sewage sludges.

S. A. RAFAY, Bangalore.

Pot experiments were carried out using activated and chemically precipitated sewage sludges as manures for the growth of ragi, potatoes, and lucern. The conditions of the crops and the yields were compared with those which had received (a) no manure, (b) farm-yard manure, and (c) nitrate of soda. Interesting results were obtained in which activated sludge and farm-yard manure compare well with each other and have proved to be superior to both precipitated sludge and sodium nitrate.

#### 20. Studies on sewage irrigation. I. Land treatment of sewage effluent and its relation to soil conditions and crop production.

S. MAHDI HASAN, S. A. RAFAY, and SUBRAHMANYAN,  
Bangalore.

On persistent application of sewage effluent, whether previously treated or not, the soil gets sticky and nonporous. Oxidation of organic matter is retarded. There are indications to show that the composition of the microflora undergoes steady change. The crops raised on such soils receive excessive supply of nitrogen almost to the stage of ripening and owing to that and, perhaps, other reasons as well, many of them either do not yield the desired products or become subject to a variety of diseases.

Vegetation trials with cereals, legumes, different grasses and a variety of market-garden crops have shown that high yields of crops of desired quality can be obtained by (a) thorough opening up of the land and application of heavy dressings of lime, followed by treatment with superphosphate, prior to sowing, (b) dilution of the effluent with 3—5 times



its volume of water prior to application, (c) use of seeds raised in distant localities and under different soil conditions, (d) rotation of crops, and (e) stopping the application of sewage and, if necessary, fallowing for a month or two whenever the soil shows signs of sickness or the yield is abnormally low.

21. The liberal use of fertilisers in the seed bed as a possible means of reducing manure bills.

B. VISWA NATH and M. SURYANARAYANA, Coimbatore.

Experiments showing the effect of different methods of manuring the seed bed on the subsequent growth of seedlings when transplanted into an unmanured soil of moderate fertility are described. The possibilities of cutting down manure bills by growing seedlings in a well prepared and manured seed bed and then transplanting the seedlings on to fields which are manured less liberally than usual, are discussed.

### PLANT BREEDING, GENETICS AND CYTOLOGY.

22. A note on the occurrence of sterility in rice (*O. sativa*).

K. RAMIAH, Coimbatore.

Sterility or failure to produce grain is one of the common causes of low returns from a crop. This is brought about by influences both environmental and hereditary. Among the environmental influences the season at which the crop is grown plays an important part.

Examination of the large number of pure line collections at Coimbatore points out that sterility is present to a very appreciable degree in a few varieties every year. Even where it is entirely absent in the parents it makes its appearance to a varying extent in the  $F_1$ ,  $F_2$ , and later generations; the more unlike the parents are with regard to their characters the greater is the sterility in the progeny. Studies on the progenies of crosses made on the Paddy Breeding Station, Coimbatore, have revealed a partial association of sterility with such characters as the presence of anthocyan pigment in particular parts of the plant, the emergence of the panicle, the duration of the plant, and the size and arrangement of the grain.

Examination of the floral parts would seem to show that sterility is mostly due to either undeveloped pollen or to its non-functioning even when well-formed. There are also a few instances where sterility might be put down as due to defective stigma.

23. Inheritance of plant height and flowering duration in rice (*O. sativa*).

K. RAMIAH, Coimbatore.

The paper deals with the inheritance studies of two important quantitative characters in rice, viz. :—the height of the plant, and the flowering duration, and the interrelationship between them and other characters, both quantitative and qualitative.

There appear to be several Mendelian factors responsible for each of these characters, and rice varieties vary considerably with regard to the factors contained in them. The contrasted pair of characters—Short and Tall, Early and Late, may form a simple pair of allelomorphs or their inheritance may be very complicated according to the factorial composition of the parents involved. The progenies of several crosses made at the Paddy Breeding Station, Coimbatore, have been followed to the fourth and fifth generations, and all the results obtained are found to come within the scope of Mendelian hypothesis.



The studies establish a very definite association between these two characters themselves. The highly significant correlation obtained is generally positive and in a few cases it is also negative. The correlation may be either physiological, or genetic, or both, but still does not go beyond the realm of Mendelian phenomena. The studies also establish a strong association of these with other quantitative characters like the length of the panicle, and the degree of emergence of the panicle, and also with certain qualitative characters like the colour of husk, and the colour of rice.

These two characters are also definitely associated with the final yield of the plant, the late and tall plants giving a bigger yield than early and short plants, the increase being proportional to the amount of difference in the characters of the parents.

#### 24. Notes on the early stages in the development of the cotton-fibre and the structure of the boll and the seed.

T. C. N. SINGH, Benares.

*Cotton-fibre*: It has conclusively been found from a microscopic study of the cotton-fibres in all the stages of development that their number does increase in the ontogeny of the fertilized ovule. This fact, however, is not in agreement with Balls' observations who maintains that there is no growth of epidermal cells into lint hairs after the first day.

*Boll*: Bolls of a large number of Indian and Indian-american cottons have been examined. It is interesting to note that in all of them thus far examined, there is one circular pit present at the very bottom of each chamber. Most of the fibres (usually of the basal region) remain firmly adhered even at maturity in these pits and also the sutures of the capsule. The attached ends of the fibres, are frequently branched like the haptera of benthos algæ. Perhaps this has something to do with the nutrition of the fibre in its development.

*Seed*: Barritt has recently shown that in *Gossypium* the 'palisade' cells are found in both the seed-coats. It is however, not the case in Indian cottons, where these 'palisade' cells occur in the outer coat only, while in *G. hirsutum*, the 'palisade' layer is much reduced even in the outer coat where it encloses the developing embryo incompletely half-way as if in a cup.

The 'palisade' cells are not bottle-shaped as reported by Barritt but instead are shaped in longitudinal sections like an hour-glass or a tumbler.

#### 25. New labour-saving compasses for measuring halo-length of cottons.

T. C. N. SINGH, Benares.

Accurate measurements of halo-length in cotton-breeding is of the utmost importance. As far as known to me, Hilson's method is the one commonly followed in nearly all the cotton-breeding stations in India. This method mainly consists in measuring the halo-length by means of a divider and then actually finding out its length in millimeters on a steel ruler. Although accurate, the strain on a worker who has to deal with a large number of specimens, is really very great. In order to remedy this, a pair of compasses has been devised by the author which gives a direct reading without the help of a ruler.

Both the limbs of the pair of compasses are provided with hard fine-pointed steel needles. A calibrated metal index in the form of an arc is fixed on one limb just a little above the steel needle, while the other free moveable limb has a fine pointer screwed on it, moving directly on the



metal index. So, as soon as the measurement is made, the pointer at once indicates the length in millimeters on the metal index.

The great advantage of this method is that besides being very accurate, it saves a considerable amount of time and strain and nearly double the work is turned out as would be done by Wilson's method.

I am very thankful to the late Mrs. G. L. C. Howard who very kindly took the trouble of getting the instrument devised by me made in England through Messrs. P. Orr and Co., Madras.

## 26. On the variation of seeds in pea (*Pisum sativum* L.).

T. C. N. SINGH, Benares.

The maximum number of ovules per ovary in *Pisum sativum* L., as far as I have been able to examine, is eight. But the maximum number of seeds (in a pod) that actually come to maturity is never more than six and commonly it is three to four. The percentage of pods with one to two or five to six seeds in any sample of a particular pea crop is rather small as compared to those with three to four seeds.

During these elaborate examinations of the variation of seeds, a very interesting point has come out, namely, in any one type of pod (one- or more-seeded) the position of the seed is not a constant character. In fact the change of position of the seed involves several permutations and combinations. The controlling factor certainly appears to be the length of the pollen-tubes which perhaps phylogenetically are of different lengths.

A study in germination of the pollen-grains of *P. sativum* is in progress.

## 27. How to increase the yield of rice in the Bombay Konkan.

V. V. GADGIL, Ratnagiri.

After describing the geographical position, rainfall, soils, and climatic conditions of the Konkan, the average outturn of rice is compared with that of other famous rice-growing tracts of India and western countries. The average of 1100 lbs. per acre is too low when compared with 5000 lbs. per acre in Spain and 3300 lbs. in Italy. How to increase the yield of rice is a great problem and it is partly solved for the trap soils of Thana and Kolaba Districts by the selection of high yielding strains of *kolamba* rice and by the judicious manuring of the crop with sulphate of ammonia. The yield of rice gradually decreases as we go from north to south from 1800 to 1000 lbs. per acre. On the contrary the percentage of straw increases in the inverse ratio. How to check this unbalanced growth is a great problem which requires special research but the methods suggested are as follows:—

(1) Crosses between rice varieties of north and south.

(2) By radical changes in manuring.

(3) By cultural methods such as wide spacing, double transplanting, etc.

(4) By the addition of green leaves instead of dry ones or farm yard manure.

The percentage of kernel to husk and the quality of seed should be invariably considered in evolving, new varieties.

## 28. A note on the castor crop in the United Provinces.

R. L. SETHI, Cawnpore.

In view of the increasing importance of the castor-oil plant, on account of its oil for lubricating purposes, attempts were made to im-



prove the varieties from the point of view of their oil-yielding properties. A few important types were isolated from a big collection made from within the province and abroad, and were sown at the Botanical Farm, Cawnpore, continuously for three years under different conditions of growth. Samples of seeds from different manurial beds and from different spikelets—smooth and spiny, dehiscent and non-dehiscent, green and mature, central and side, etc., were taken, and the results of their analysis are compared. A general description of the cultivation of the crop at present existing in the province, with recommendations for improvement based on above results is also given.

29. A preliminary note on the occurrence of sepaldoidy and sterility in Til (*Sesamum indicum*).

S. C. Roy.

30. Inheritance of grain color in ragi, *Eleusine Coracana* Gaertn., and the relation of grain color factors to plant purple pigmentation.

G. N. RANGASWAMI AYYANGAR and U. ACTHYUTHA WARIYAR,  
Coimbatore.

Two factors  $B_1$  and  $B_2$  seem to be responsible either alone or together, in producing the brown pigment of the testa, characteristic of the Ragi grain. In the absence of the B factors, the grain is white. All the white grained varieties consist of plants which are green throughout. Some of the white grained plants carry a factor B which in association with either or both of the B factors in a green throughout, produces a purple pigmented plant. This accounts for all purple pigmented plants bearing only brown grains.

31. Agricultural characteristics of Indian and American cottons.

G. L. KOTTUR, Dharwar.

The characteristics of Indian and American cottons were studied under the same field conditions. American cottons are on the whole least vegetative, early, rapid growing, immune to fusarium wilt but highly susceptible to the attack of insects. The value of American staple and its possibilities are discussed. In view of the many failures which American cottons have sustained in this country the breeding of suitable Indian cottons is recommended to replace the present unpromising types.

32. Problems of rice-breeding with special reference to Bihar and Orissa.

M. ALLAM, Sabour.

In discussing the problems of rice-breeding, the general principles of plant-breeding that are involved in this are first pointed out and then some of the most important problems of rice-breeding such as isolation of pure lines, non-adaptability of the crop to varying conditions of soil and moisture, physiological study of the rice plant and similar other problems are taken up and the lines of work to be adopted in future are pointed out.

The question of the classification of cultivated rices has also been considered and the old controversy about basing our classification on grain characters alone or on both the agricultural and grain characters has been discussed in some detail on the basis of observations made at



Sabour and those by other workers in foreign countries, especially in Japan. From this discussion it is concluded that some of the agricultural characters, though less constant than the grain characters, are of special practical importance and they must always be included in any scheme of classification of the cultivated rices. In discussing this question a number of rice-breeding problems have also been considered.

The last portion of the paper deals with such questions as appropriate spacing of the transplanted paddies, its effect on the tillering of the crop, and the difficulties that accompany breeding of a crop for quality. Finally an interesting discussion on the factors that determine yield in paddy has been taken up and it is proposed to make a complete analysis of what actually constitutes the yielding capacity of a crop. Closely related to yield is the problem of "sterility". Various forms of sterility that are reported to occur in this crop are also considered and measures to check them are suggested.

### 33. Notes on the classification of Surma valley rice.

S. K. MITRA and P. M. GANGULI, Jorhat, Assam.

The need for a general classification of rice has long been felt from all quarters. The value of an agricultural classification which mainly depends on the water requirements and the time of flowering and ripening of grains can hardly be overestimated. But this does not satisfy the requirements of a true classification. Both Kikkawa and Graham have advocated the grain characters as the only satisfactory basis for a general classification. In their work on rice the writers have classified 602 types of Surma Valley rices into 104 groups according to the grain characters, such as the size of grain and the colour of inner glume and kernel.

## PLANT PHYSIOLOGY.

### 34. On the effect of potassium permanganate on the growth, flowering, and fruiting of gram (*Cicer arietinum* L.).

T. S. N. SINGH, Coimbatore

The author has performed series of experiments in which gram seeds were germinated in cultures, irrigated with a solution of potassium permanganate (.5 gr. to every 2 oz. of water); and a close study has been made of the changes that took place in the ontogeny of the plant in response to the addition of potassium permanganate to the soil.

The following results have been obtained in the case of the experimental cultures as compared with the controls which were also irrigated simultaneously with an equal measured volume of ordinary water :—

- (1) Quicker germination.
- (2) Much darker green leaves.
- (3) Longer root-system.
- (4) Earlier bud formation.
- (5) Earlier flowering.
- (6) Earlier fruiting.

There was, however, no difference in length of the aerial portions.

### 35. On the absorption of water by the seed-coat of gram.

B. N. SINHA and C. M. SINHA, Bhowali.

Two types of grams (a) yellow-brown type, and (b) deep-brown type obtained from Central India were experimented upon. It has been



found that both in soaking and germination-tests the Deep-brown type behaves much better than the yellow-brown type. The germination curves of both the types are double-humped showing thereby two maxima during germination. Remarkable was the case of a yellow-brown type which took full 1512 hours to be fully soaked, after which it germinated normally. Also cases were found not unusually in both the types but more so in the yellow-brown type which took 2-11 days to be fully soaked. Afterwards when subjected to germination tests, they behaved quite normally.

Conclusion has been arrived at that apart from specific or varietal differences there does also exist difference in the seed-coats of even the same variety so far as the soaking tests are concerned.

### 36. Some preliminary studies on the effect of various temperatures on the root absorption in American cottons.

J. C. LUTHRA and GHAS-UD-DIN, Lyallpur.

The partial failure of American cottons which has been occurring in the Punjab for several years presented a very intricate problem for investigation. The various causes to which the ill-health of the plant could be attributed were insect pests, fungoid diseases, and physiological disturbances in its metabolic activities.

White fly has been considered in some quarters to be mainly responsible for the trouble, but no definite conclusions have yet been arrived at with regard to the extent of damage caused by it, partial failures of the crop having been noticed even when white fly is practically absent. As regards fungoid diseases, no particular parasite has been found on affected plants. In the absence of any definite causal organism it was thought that some physiological derangement in the plant might account for its unhealthy condition which generally arises towards the end of August. The high summer temperature of the Punjab plains is obviously one of the most striking environmental factors that govern the life processes of the cotton plant. Attention was, therefore, directed to the study of the effect of temperature on root absorption which is a vital physiological process. In this connection it was observed from the soil temperature records of Lyallpur that the maximum temperature of the soil at a depth of 30 c.m. was about  $37^{\circ}\text{C}$  in August and that the general range of soil temperature between May and November was  $20^{\circ}\text{C}$ — $36^{\circ}\text{C}$ . Very few data are available on the subject. The only previous investigations on cottons are those of Balls in Egypt, but Eckerson, Delf, Stiles and Jorgensen, have studied the influence of temperature on the permeability of protoplasm. The experiments reported in this paper relate to the determination of the rate of root absorption by 285F, and 4F, Punjab-American cotton plants grown in water culture at different temperatures. The water culture jars were kept in water-baths in which the temperature was maintained at 10, 15, 20, 25, 30, 35, and 40 degrees centigrade respectively. Each culture jar had a graduated tube in c.c.'s. The results obtained indicate that the rate of absorption increased steadily with the rise of temperature from  $10^{\circ}\text{C}$  to  $25^{\circ}\text{C}$  with an average of increment of about 64%. Above  $25^{\circ}$  and up to  $30^{\circ}$  the increase amounted to about 10 per cent. only. From  $30^{\circ}$  to  $35^{\circ}$  the rate went up to over twice the initial amount recorded at  $10^{\circ}$ . The plants kept at  $40^{\circ}$  showed an increase of about 17 per cent. more than those at  $35^{\circ}$ . Experiments conducted in 1929 showed that above  $40^{\circ}\text{C}$  root absorption began to slow down. Total root absorption for a period of 6 hours daily from 12 noon to 6 p.m., has been calculated on basis of 2,000 square centimeters of leaf surface and 1 gramme of dry matter of roots.

Graphs illustrating the daily increase of root absorption in the 7 sets of experimental plots are given in the paper.



## 37. Determination of temperature of plants.

J. C. LUTHRA, Lyallpur.

Variations of air temperature exercise a great influence on the growth of farm crops. It is important to ascertain the exact relationship between the temperature of the air and that of the plant both within the tissue and at the surface of the organs. The leaf of the cotton plant was considered to be the most suitable part for these studies and the temperature of its surface and of the internal tissue in the midrib and petiole were determined. The apparatus employed consists of a thermo-couple arrangement specially modified from that used by some American workers.

Details of the methods of calculating temperature in degree from galvanometric readings are described in the paper. Readings of the air and the plant temperatures were taken thrice daily at 7 A.M., 1 P.M., and 7 P.M., respectively. On account of rapid fluctuation of the air temperature at least six observations are taken at a time and the average was recorded. The temperature of the leaf was found to be influenced by (1) temperature of the air, (2) moisture in the soil, and (3) age of the leaves.

A close correspondence in the temperature of the plant as shown by that of the leaf, and the surrounding air has been revealed by the results. Plants do not seem to have any normal sap temperature corresponding to the normal temperature of animals, but their temperatures rise or fall with that of the air. Generally, however, in the afternoon the plant is cooler than the air by about  $2-4^{\circ}\text{C}$ ; in the morning and evening the difference is very slight.

## 38. Studies on the metabolic activities in grape berries from the time of bearing to maturity.

J. C. LUTHRA and I. S. CHEEMA, Lyallpur.

Investigations on the subject comprised chiefly the quantitative estimation of the rate of respiration of the berries of two known Peshawar varieties of grapes Jaishi and Tur grown in the Lyallpur botanical area for a number of years. Respiratory activity was determined on grape bunches removed from the plants as well as on those *in situ* attached to the plants. Besides this, total amount of reducing sugar, titrable acids and nitrogen contents were determined.

*Results :—*

a. Experimental data show that berries respired very actively during the early stages of their growth, but the intensity of respiration slowed down as the berries advanced in age.

b. There is a definite correlation between sugars and respiratory activity. The co-efficient came to  $-0.52 - 0.14$  and was significant.

c. Reducing sugars show a steady increase with the ripening process. The maxima in the curve for sugars corresponds with the complete maturation of the grape berries.

d. Total titrable acids go on increasing for about four or five weeks and afterwards they begin to fall. The maxima in the acid curve coincide with the accumulation of sugars in much greater amounts than before.

e. Nitrogenous contents show a straight decline till berries were 47 days old. Afterwards there was a slight increase.

f. Specific gravity of the grape juice follows closely with the increase of sugars.

g. Starch was not found at any stage of the growth of the grape berries. It appears that sugars are directly formed probably from acids.



## 39. Notes on a few cultural experiments on rice.

S. K. MITRA and P. M. GANGULI, Jorhat, Assam.

The results of experiments covering a period of ten years are summarised as follows :—

- (a) Deep ploughing gives a better outturn than shallow ploughing especially in broadcast *aus* (autumn paddy).
- (b) Heavy seeds, selected by the specific gravity method do not give any appreciable increased outturn.
- (c) *Aus* paddy thrives well at Karimganj when sown from April to June, while the best time for transplanting *Sail* (winter paddy) is from the latter part of July to the end of August.
- (d) Seedlings of *Sail* left over in the seed bed for more than five weeks show a decided decrease in yield.
- (e) Two seedlings per hole transplanted 6 inches apart for *Aus*, 9 inches apart for *Sail*, and 12 inches apart for *Asra* (shallow water Aman) paddies have been found to give the best result.
- (f) Stronger seedlings do not show a material advantage in yield over weaker ones, but they have physical and mechanical strength enabling them to withstand the attack of insects or the rush of flood water in the early stage of growth.
- (g) Weeding in proper time gives a greatly increased outturn especially in broadcast *Aus* paddy.
- (h) Other conditions being equal all *Sail* varieties of paddy yield most when they have about a foot of water at the base during the growing period.

## 40. The chemical study of the effect of frost on the cane-crop.

V. G. PATWARDHAN and N. G. APTE, Poona.

In the Ahamadnagar district along the Godavary and Pravara canals, a cold wave passed over the cane-crop in 1929 causing great damage.

A chemical study was undertaken to investigate the changes in the constituents of the cane juice as an after-effect of frost in the case of affected and unaffected plants and first ratoon canes, and affected *Adsali* (July planting) cane. Six trials were taken with an interval of three days for the first three trials and an interval of seven days for the last three trials. The *Gul* was prepared under different conditions.

Thirty-three experimental tests were taken under controlled conditions and many other affected areas.

The result showed that there was :—

	From	To.
a. Increase in glucose (reducing sugars) ...	1 to 1.5%	1.2 to 2.5%
b. Decrease in sucrose (non-reducing sugars) ...	18	8 to 15%
c. Decrease in Brix reading (total solids) ...	18 to 20	13 to 20
d. Decrease in purity-(ratio of sucrose to total solids) ...	86 to 92	45 to 90
e. Not much variation in acidity from the normal.		

Experiments were conducted to find out a method of preparing solid *Gul* from frost-affected canes by judicious application of clarifying agents like lime-water, soda, *Sajji*, and *Bhendi* (*Hibiscus esculentus*) extract, thus separating the scum completely. It was found possible to prepare marketable *Gul* from frost damaged canes.



**AGRICULTURAL ECONOMICS AND STATISTICS.****41. Studies in the cost of production of farm produce.**

P. C. PATIL, Poona.

*Importance and objects* :—Cost studies are important to the producer, consumer, and government. Farmer likes to spend less and get more; consumer likes to get the full value of his money; government wants cost-data for tariff, international trade and, agricultural finance considerations. Cost studies are essential for improving farm organization.

*Kinds of enquiries* :—Survey method and route method of study. In the survey method estimates of costs and receipts are collected by sending questionnaire forms. Survey method is not suited for Bombay conditions, except for sugarcane on canals and cotton in Khandesh. In route method investigators record information every week or so. Route method is useful both for studying crops and farms.

*Measure of income* :—In U.S.A. investigators aim at "Labour income" i.e., annual wage earned by the farmer for his labour after allowing all possible expenses including rent, depreciation, interest and even wages for the labour of the family members. In England, investigators try to find what "profit" the farmer makes on his outlay, allowing for every cost including wages even of the members of the family. These income measures are not suited to Indian conditions. I have adopted two different income measures (a) 'Family labour income' i.e., the annual wages, the whole family makes. This means total receipts minus all operating expenses, except wages of home labour; and (b) 'Farm business income' which means the difference between the value of the gross produce and only the out-of-pocket expenses. I learn that the measures proposed by me are practically similar to those proposed by Dr. Laur of Switzerland in the International Congress of Agriculture at Bukharest. What I call 'Family labour income' and 'Farm business income' are called 'Family labour earnings' and 'Family farm earnings' by Dr. Laur.

*Crop Study* :—In crop study we should try to find costs, receipts, and net profit.

*Farm studies* :—In the farm study we should find family labour earnings and family farm earnings.

The details of costs by operations and yields together with receipts supply, in both kinds of studies, sufficient material for improving farm efficiency.

**42. Statistical uniformity in the presentation of experimental results in agriculture.**

VAIDYANATHAN, Delhi.

*Introduction*—The different kinds of the agricultural experimentation—the modern field technique and its requirements based upon the system of replication—the need for indicating the accuracy of the field experiments—an examination of the details of the meteorological records and the method of recording them—an examination of the method of recording rotation and replication experiments, involving the details of the system of replication, the nature of the trial and the summary of the results—illustration from the Rothamsted experimental station.

**43. Agricultural Insurance.**

J. C. GULERI, Lyallpur.

No serious attention has so far been devoted in this country to the subject of agricultural insurance. Cattle insurance has been tried and with a few exceptions pronounced to be a failure. Only spasmodic, and consequently, uninspiring efforts have been made here and there to



try other forms. The idea is, however, full of immense potentialities in the peculiar circumstances of this country.

Considerable progress has been made in this direction in other countries and if the movement is closely followed, agricultural insurance would become a necessary adjunct of the co-operative movement and agricultural development, both of which would receive a much-needed stimulus thereby. Spasmodic and half-hearted attempts are bound to fail but it should be possible to try, in carefully selected localities with necessary propaganda and organisation, insurance of the various risks to which the farmer is exposed, viz., crop failures, loss of cattle and buildings and even low prices, and if this is successful, the psychological effect on the farmer would be tremendous.

Insurance schemes should consequently be worked out to suit particular localities and should be definitely associated with the administration of Land Revenue, Famine Relief and Taccavi loans and worked by special organisations (Insurance Boards or Commissions) with the fullest collaboration of the Co-operative, Agriculture, Veterinary, and other beneficent departments concerned.

The movement would go a long way to allay rural discontent and would specially appeal in times of depression such as the present and as it spreads, a strong impetus will be given to the development of rural credit, agricultural improvement and village uplift.

#### 44. The methods of the grain markets in Northern Central Provinces.

P. D. NAIR, Nagpur.

The northern districts of the Central Provinces, comprising the plateau and the intervening valley of the Nerbudda, constitute the most important grain-producing tract of this province. Nearly two-thirds of the grain exported from this province comes from this tract alone. The famous markets of Kareli, Gadarwara, Itarsi, Harda, Banapura, Jubbulpore, and Sihora situated on the main railway lines attract the surplus produce of the outlying areas. The large volume of produce that comes into these markets is first sold there to local merchants and commission agents who subsequently export it to places outside the tract. The total quantity of business done in these wholesale markets during the busy months of April, May, and June, will amount to several lakhs of rupees. Some important questions connected with this marketing of grain, such as, who brings the grain to the market, how the grain arrives, the methods of sale, the part played by the middle men and commission agents, the expenses of marketing and the weights and measures used in these markets are discussed in this paper.

#### 45. The marketing of oranges in Nagpur.

P. D. NAIR, Nagpur.

The "Santhras" or oranges of Nagpur have an all-India reputation. During the season these delicious fruits can be seen in the bazars of most Indian cities. The production of and trade in oranges appears to be a growing business in the Nagpur district and the opening of the new railway lines to Itarsi and Kazipet has further extended the market for this commodity. It is possible to form an idea of the importance and magnitude of this trade in oranges from the fact that during the season of 1927-28, no less than 41,450 carts or roughly 103,625,000 oranges arrived in the Nagpur market and the Nagpur Municipality derived an income of Rs. 35,269 from this trade. There is another market for oranges at Katol—a place about 30 miles from Nagpur on the Itarsi line, and oranges are also exported directly from several places situated along



the Nagpur-Itarsi line. The total value of the oranges exported annually from the Nagpur District will amount to several lakhs of rupees. A detailed investigation into the marketing conditions of this fruit was undertaken by the writer during the last season. Several interesting points like the method of sale in the market, the financing of the trade, the packing of fruits, the method of transporting fruits, etc., etc., are discussed in the paper.

### **ANIMAL HUSBANDRY (INCLUDING PASTURES).**

46. A preliminary note on the effect of manures on the yield and composition of grass lands at the Dacca farm.

F. J. GOSSIP *and* D. DUTTA, Dacca.

This is just a note on the work undertaken by the writers to see whether pasture lands can be improved by the application of different manures either as regards yield or the composition of the flora of the same. The results of the first year's work show that artificial farm-yard manure increases the green matter and the floristic composition is also changed. As the Dacca farm soils are more or less acid, liming has a beneficial effect on the increase of the herbage.

47. Rock salt and its use to grazing animals.

L. B. KULKARNI *and* L. G. ANNIGERI, Poona.

1. The provision of salts to animals on the grazing area is a novelty in Western India. Grazing animals, however, get it in slight quantity by licking rocky soil, ashes and the bodies of other animals.

2. Rock salt has been found more convenient for supply to grazing animals since it is in compact crystalline mass and is less hygroscopic than other forms of salt.

3. Animals consume more salt during stall feeding than in open grazing. They consume more when feeding on poor stuff than with green succulent growth.

4. Salt is greatly relished by all bovines who forget the habit of licking rocks, soil, ashes and the bodies of other animals when salt licks are provided.

5. Salt facilitates easy control of animals.

48. A note on the introduced fodder crops at the Dacca farm.

D. DATTA, Dacca.

For the last few years the department of agriculture, Bengal, has been paying some attention to the introduction of suitable fodder crops for Bengal.

Juar and maize are the two main fodder crops in Bengal already under cultivation; as the Juars take a very long time for maturity, the department has been trying to introduce early types and we have been successful in acclimating two of the American Sorghums. These are already in demand.

Maize which is also a heavy yielder is grown largely in Northern Bengal. Experiments for the last two years show that the heavy yielding Kalinpong Maize can be replaced by some of the heavy yielders ensilage corn of the States of America.

As regards permanent fodder crops, the field has so long been held undisputedly by the Guinea grass, but under Dacca farm conditions we



find it displaced by Napier grass *Pennisetum purpureum*. We may mention that another grass viz., Natal grass *Tricholaena rosea* is a good second to Guinea grass.

We find difficulty in growing a Rabi fodder grass and we find Sudan grass *Holcus sudanesis* serves our purpose.

There are various other grasses under observation and one of them has been found to remain ever-green throughout the hottest months at Dacca. This is being worked out in detail.

#### 49. Preliminary note on the composition of the pasture lands of Bengal.

K. BISWAS and D. DATTA, Calcutta.

The composition of grass lands of the different parts of Bengal, the Calcutta maidans, the lawns of the Royal Botanic Gardens, Calcutta, and the fields of Dacca farm attracts our attention for some time. Observations on the growth of individuals of different species as also the species as members of a community, have been made and data are still being collected for the investigation of the periodicity and rotation of the various species forming a meadow or a grass land. As a rule, *Imperata arundinacea*, *Cynodon dactylon* associated with a few species of *Panicum* and several species of *Cyperaceae* such as *Cyperus rotundus*, *Killingia monocephala* and a few *Fimbristylis* species are the predominant species of a grass land in Bengal. These grasses and sedges are in almost all pasture lands intermixed with a carpet formation closely adhering to the soil of a few species of *Dicotyledons* such as *Evolvulus nummularis*, *Desmodium triflorum*, *Bonnaya brachiata*, *Alysicarpus vaginalis* and *Indigofera linifolia* and a few others. The study of the life history of these weeds and other taller weeds in rotation to the grasses at different seasons of the year forms also a part of the present paper. Experiments have been undertaken by one of us to investigate the comparative merits of these grasses and weeds as fodder crops. It may be noted that some of the American grasses introduced in this country replace the indigenous grasses and are also suitable as fodder grasses. The question will be discussed from an agricultural standpoint in a subsequent paper.

### FRUIT GROWING.

#### 50. The bearing of the "Alphonso" mango in the Konkan and some methods of regulating the same.

P. V. WAGLE, Ratnagiri

The Alphonso is a shy bearing variety of mango but still it is getting very popular on account of its other desirable qualities. Of the several factors which affect the bearing, spacing seems to be an important one. Closely planted trees produce a smaller number of fruits and bear less frequently and thus the outturn is considerably reduced. The quantity and distribution of rainfall and the temperature have much to do with the bearing but these are factors beyond control. The bearing, however, depends much upon the production or otherwise of fresh vegetative shoots in October. Trees producing October shoots generally do not bear during the following season as the shoots do not get sufficient time to be mature enough. The pruning of the fresh vegetative shoots some time from the middle of November to the end of February leads to the development of the dormant buds on the lower mature wood into flower-heads which yield an almost normal crop of mangoes. Manuring with sulphate of ammonia and farm yard manure in June helps the maturity of the October shoots and thus induces the trees to bear in successive years instead of in alternate years.



## 51. Cold storage of fruits. Part I. Mangoes.

D. V. KARMARKAR and B. N. BANERJEE, Bangalore.

It has been found that "Badami" and "Pyri" (best table variety) mangoes obtained locally, could be preserved in a cold room at 0°C. for about 40 days in good condition. Firm and mature mangoes in cold storage become soft in about a week's time, but do not ripen afterwards. Micro-organisms responsible for the decay have been isolated, and their characteristics studied. They are found to be generally, (a) a fungus which persists even under anaerobic conditions, and (b) a bacterium which thrives under aerobic conditions only. Preliminary treatments like washing with antiseptic solution or blanching do not show any special benefit.

## 52. Notes on the periodic nature of the yield of the mango crop in Bihar: with hints on the probable cause thereof and suggested remedies.

M. N. GHOSH and B. G. DAS, Sabour.

Plotting of the crop records for ten years at Sabour indicates that the yield of mango gives rise to a periodic curve, having a period of six years. The form of this curve and its connection with seasonal and climatic conditions are discussed. The relation between the rainfall in the previous monsoon season and fruiting is discussed from the past ten years' records. A connection between fruiting and the weather at the time is sought to be established. Results of manuring and watering, together with certain treatments with a view to the maintenance of energy and of the carbon-nitrogen balance, are mentioned. Finally, the heredity of the tree for successful fruiting is described.

**PLANT DISEASES AND PESTS.**

## 53. The coccidæ of the prickly pear in South India and their economic importance.

T. V. RAMAKRISHNA AYYAR, Coimbatore.

It is common knowledge that in South India, except in a few tracts like the West Coast, the prickly pear (*Opuntia*) enjoys a very wide distribution all over the plains. In districts like Tinnevely, Madura, Trichy, and Coimbatore it is found growing luxuriantly covering acres and acres of arable and pasture lands and levying a substantial toll on the farmer every year to keep it within certain bounds. The problem of the disposal of this plant either by utilisation or by destruction has been engaging the attention of the public and the authorities for the past many decades. One of the control measures tried in this connection has been the use of the natural enemies of this plant. Among these latter, the most important are insects belonging to the Family Coccidæ which includes scale insects and mealy bugs. For over ten years in the past the writer has been paying some attention to the systematics and bionomics of South Indian Coccidæ and during the course of such investigations he has had chances of observing and studying insects on the different species of *Cacti* found growing in the country. In view of the fact that a foreign prickly pear Coccid has gained entry into the country recently it is thought that a paper on the subject may not be inopportune. In this paper, an attempt is made to record the results of the writer's studies of the Coccidæ of the prickly pear and their economic importance and at the same time to review briefly the previous attempts in the control of prickly pear by insect agency.

The paper begins with a few remarks on the pest condition of prickly pear in South India and the different kinds of the *Cactus* found growing



in the province. Then follow short descriptions and bionomical notes on the different species of prickly pear Coccids and then the economic importance of the latter is described. The importance of the paper mainly centres round the recently introduced Cochineal insect *Dactylopius tomentosus* L. which is found to do remarkable work in controlling the common prickly pear in some of the southern districts of Madras. The paper concludes with some remarks on the possibilities of these introduced Cochineal insects as factors in the biological method of pest control and with a few suggestions in that connection.

54. Preliminary studies in the destruction of Potamogeton (Sirwal) in canal beds.

H. N. BATHAM, Cawnpore.

Potamogetons are submerged water-plants with creeping root-stocks and leaves submerged or floating alternate, mostly entire and intrafoliaceous stipulate. There are several species, those found commonly in the canals of United Provinces, are either *P. Indicus* or *P. pectinatus*. They are termed *sirwal* or *sewar* in vernacular.

The growth of potamogeton (Sirwal) is common in nearly all the canals of the United Provinces, and is ignored so long as it does not give any trouble. In some of the canals of Rohilkhand, however, its growth has been known to become so profuse that the actual discharge of the water was reduced to one-third of the theoretical discharge.

Mechanical means of eradication by excavating about six inches of earth from canal bed was first tried in the hope that the root-stocks of the weed would also be removed but this did not prove effective and the plants grew again as vigorously as before.

Next it was decided to try chemical means for destroying the weed.

Arsenite preparations have been used in Bengal for destroying water hyacinth, which is very different to Potamogeton. Moreover it would be dangerous to spray the canal with poisonous chemicals as the canal water is used for domestic purposes as well as for irrigation. It was therefore desired to use such chemicals which will not be poisonous to animals. Accordingly quick-lime was tried. The experiments with lime have shown that the application of unslaked lime at the rate of 2 maunds per 100 sq. ft. is quite effective in destroying the potamogeton completely and that smaller quantities are only partially effective. It has still to be seen how long the action of quick-lime remains effective in checking the growth of Sirwal. The study of the use of other non-poisonous chemicals to destroy the weed and of mechanical means of checking its propagation is being continued.

55. Mechanical versus biological control of the predators and parasites of lac insects.

P. S. NAGI, S. N. GUPTA, and M. P. MISRA, Namkum.

The paper discusses the inter-relationship of the lac insect and insects predatory and parasitic on it. This relationship is further complicated by the existence of alternative hosts of the insects predatory and parasitic on lac, and of the friends of the lac-insect including predatory, parasitic, and hyper-parasitic insects.

A brief *rèsumé* of the life histories of the more important insects discussed in the paper is given.

The use of predator, parasite, and hyper-parasite friends of lac in the biological control of lac enemies is discussed.

An account of mechanical control methods of lac enemies is given.

The conclusion is that, at the present time, mechanical methods of control are recommended as of primary importance and biological methods as of secondary importance in the lac industry.



56. The eelworm disease in garden plants. I. *Hibiscus esculentus* Linn.

A. B. SARAN, Cuttack.

The cause of chlorosis in *Hibiscus esculentus* growing in the laboratory garden has been studied. The chlorotic plant had numerous tubercles on its roots, which when investigated, were found to contain eelworms at various stages of development.

These eelworms seem to—

- (a) destroy the rootlets and thus decrease the absorbing system,
- (b) damage the conducting system of the plant,
- (c) disturb its metabolism, as indicated by excessive production of calcium oxalate crystals in the tissues.

All this must be leading to insufficient supply of the necessary elements to the plant which, as a result, becomes chlorotic and the topmost portion crumples and dries up.

Some remedial measures are being tried.











# INDIAN SCIENCE CONGRESS.

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ABSTRACTS OF PAPERS.

Section of Chemistry.

*President :—Prof. K. G. Naik, M.A., D.Sc., F.I.C.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Chemistry.

### *Abstracts.*

1. Homology and isomorphism of monofluophosphates with sulfates.

P. B. SARKAR and H. C. GOSWAMI, Calcutta.

In continuation of our previous work on the isomorphism of fluoberyllates with sulfates we have found another anion, viz., monofluophosphanion analogous to sulfanion.

Simple monofluophosphates double salts and alums have been prepared isomorphous with the corresponding sulfates.

2. On the chemical and spectroscopical examination of some Indian rare earth minerals, e.g., samarskites from Gaya and Nellore.

P. B. SARKAR, Calcutta.

3. Use of hexamethylene tetramine as an analytical reagent.

P. RÂY and A. CHATTOPADHYA, Calcutta.

In extension of our previous work on the estimation and quantitative separation of iron from zinc, manganese, nickel and cobalt by hexamethylene tetramine, it has been found that the latter can be used with advantage for the gravimetric estimation of aluminium, uranium, zirconium, titanium and thorium, as well as, for their quantitative separation from most of the bivalent metallic elements like zinc, manganese, nickel, cobalt and magnesium. Even in the case of individual determinations hexamine has got advantages over ammonia in the fact that no special precautions need be taken for having the reagent free from carbondioxide and silica as is necessary when ammonia is employed.

4. Studies on arseno oxalic acid and its salts.

T. P. BARAT, Calcutta.

It is known from a study of the various organic compounds of arsenic that it can function as a centre of dissymmetry in the pentavalent state. It is interesting to find whether trivalent arsenic can also behave as the same. There are several contradictory statements as regards the existence of arseno oxalic acid and its salts:—c.f. Bergmann, Souhay and Lanseen (*Lieb. Ann.*, 105, 55) and Rosenheim (*Z. Anorg. Chem.*, 1899, 20, 305). The point of interest as regards these compounds lies in the fact that if the acid be of the hexa co-ordination type, it can be resolved into its optically active components. Several attempts were made to prepare the pure acid by crystallising  $\text{As}_2\text{O}_3$  from equimolecular and excess concentrations of hot solutions of oxalic acid, but without success. Accordingly, the equilibrium of the ternary system  $\text{As}_2\text{O}_3$ — $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{O}$  has been studied at  $30^\circ\text{C}$ . The solid phases that are in equilibrium with various saturated solutions are  $\text{As}_2\text{O}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $2\text{H}_2\text{O}$  and a mixture of the two. Studies on arseno oxalates will be shortly taken up, and interesting results are expected.



## 5. The decomposition of ammonium nitrate.

M. S. SHAH and T. M. OZA, Ahmedabad.

The decomposition of ammonium nitrate has been studied quantitatively by heating the dry substance in vacuo and analysing the gas evolved and the mass left at the end of each experiment.

Experiments were conducted to examine the effect of changes in (a) pressure, (b) temperature, (c) mass, and (d) time of heating. The influence of (i) thoria, (ii) anhyd. sodium sulphate, (iii) anhyd. copper-sulphate, and (iv) arsenic acid on the mode of its decomposition was also studied at various temperatures.

The results show that

1. ammonium nitrate first dissociates and ammonia is evolved acc. to  $\text{NH}_4\text{NO}_3 \rightleftharpoons \text{NH}_3 + \text{HNO}_3 \dots \dots \text{A}$ ;
2. the dissociation is followed by oxidation of ammonia with nitric acid in the gaseous state and some nitrogen is produced. As the increase in nitric acid concentration favours this change it appears that the following reactions occur  

$$\begin{array}{l} \text{NH}_3 + 3\text{HNO}_3 \rightarrow (\text{N}_4\text{O}_6 + 3\text{H}_2\text{O}) \rightarrow 4\text{HNO}_2 + \text{H}_2\text{O}, \\ 4\text{NH}_3 + 4\text{HNO}_2 \rightarrow (4\text{NH}_4\text{NO}_2) \rightarrow 4\text{N}_2 + 4\text{H}_2\text{O}; \\ \hline 5\text{NH}_3 + 3\text{HNO}_3 = 4\text{N}_2 + 5\text{H}_2\text{O} \dots \dots \text{B}; \end{array}$$
3. both A and B lead to an increase in the acidity of the residual mass. When nitric acid is present in quantity nitric oxide and nitrogen peroxide are evolved along with nitrogen;
4. the main product of decomposition in all the experiments is nitrous oxide. It seems highly probable that this is produced by the decomposition of molten ammonium nitrate.

## 6. The determination of mechanical wood pulp in paper by Cross and Bevan's volumetric method.

KISHEN LAL, KISHEN PRASAD, H. D. SURI, and H. B. DUNNICLIFF, Lahore.

The effect of temperature on the absorption of phloroglucin and the effect of concentration of the phloroglucin and the total amount of the reagent required to obtain constant results, have been studied. The reaction probably consists of absorption superimposed on chemical action. Very precise and carefully controlled conditions specified in the report are necessary to obtain consistent results.

## 7. The rapid determination of small quantities of silver in commercial products.

H. B. DUNNICLIFF, Lahore.

This volumetric method depends for its end point on the appearance of a cloudy layer of silver bromide as observed in a specially designed apparatus.

## 8. The action of nitric oxide on hydrogen sulphide in the presence of excess of water.

SARDAR MOHAMMAD, JAI KISHEN, and H. B. DUNNICLIFF, Lahore.

(1) The main products are ammonium thiosulphate, ammonium nitrite, sulphur, nitrous oxide and nitrogen.

(2) Nitric oxide decomposes ammonium sulphide forming poly-



sulphides of ammonium, small quantities of ammonium thiosulphate, nitrous oxide and nitrogen. Excess of nitric oxide increases the yield of nitrous oxide. Excess of ammonium sulphide gives pure nitrogen.

(3) Saturated hydrogen sulphide solution reduces nitrous oxide quantitatively to nitrogen and ammonia.

(4) Nitric oxide slowly oxidises dilute solutions of ammonium thiosulphate to ammonium sulphate.

(5) Explanation of these reactions are given in the paper.

### 9. The detection and determination of impurities in commercial linseed oils.

H. B. DUNNICLIFF, MAHAN SINGH, *and* DARA SINGH, Lahore.

The process suggested depends upon (1) the drying of the oil (oxygen absorption value), (2) the insoluble-oil-bromide value, and (3) the saponification value.

It has been shown that the insoluble bromide number can be used for the determination of the percentage of adulterant in certain cases.

A system for the examination of commercial linseed oils has been suggested.

### 10. A suggestion to reduce water softening expenses in dye-houses by using effluent water to feed the boilers.

S. V. SHAH, Kolhapur.

In certain cases boiler feed waters are very hard even, as much as, 60 degrees. Certain operations during dyeing like boiling the yarn in water alone or with soda ash or with soap, incidentally soften the waters. It is suggested here that such waters instead of being run out, should be allowed to settle and after filtration should be used as boiler feed waters, thus rendering the expenses for softening unnecessary.

### 11. Micro-analysis of hydrides and halides of sulphur dissolved in benzene.

B. SANJIVA RAO *and* M. R. ASWATHNARAYANA RAO,  
Bangalore.

During certain investigations on sulphur chloride and bromide solutions in benzene a method of micro-analysis of a mixture of hydrogen sulphide, persulphide, free sulphur, and sulphur halide in benzene solution was developed. Pure dry hydrogen is passed through the mixture and the hydrogen sulphide liberated is absorbed by zinc hydroxide emulsion and estimated colorimetrically using p-amino dimethylaniline sulphate. On removal of the free  $H_2S$ , the benzene is shaken with pure mercury in an atmosphere of  $H_2$  and the  $H_2S$  liberated by the decomposition of the persulphide estimated. The  $HgS$  formed (which corresponds to  $\frac{1}{2} H_2S^2 + \text{sulphur halide} + \text{free sulphur}$ ) is decomposed by  $HI$  and the  $H_2S$  evolved determined. The chloride or bromide in solution is separately estimated as silver salt by Pregl's method, after fusion with alkali carbonates to oxidise sulphur to sulphate. Data required for the estimation of each of the constituents of the mixture is thus obtained.

### 12. Micro-analysis of mixtures of sulphide and sulphite of alkalis.

B. SANJIVA RAO *and* M. R. ASWATHNARAYANA RAO,  
Bangalore.

Through the mixture of alkali sulphide and sulphite contained in a flask  $H_2$  is passed to expel air, phosphate buffer of pH 6 is added and



the  $\text{H}_2\text{S}$  liberated is completely removed by a current of  $\text{H}_2$  and estimated colorimetrically using the diamine reagent. The sulphite in the flask is then estimated iodometrically.

A mixture of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  solutions in dry benzene is analysed by shaking with an aqueous solution of baryta in an atmosphere of  $\text{H}_2$ ;  $\text{CO}_2$  is then passed till solution attains pH 6 and the  $\text{H}_2\text{S}$  liberated is estimated as indicated above. The barium sulphite in the flask is oxidised with hydrogen peroxide and estimated as sulphate by Pregl's method using a micro-Neubauer crucible.

13. Reaction between iodine and hydrogen sulphide in dry benzene solution.

B. SANJIVA RAO, Bangalore.

In dry benzene, iodine reacts *very slowly* with hydrogen sulphide to form hydrogen persulphide and some sulphur iodide (cf. Parsons J.A.C.S. 47, 1820). The effect of water on the reaction is discussed.

14. On a colloidal theory of matter.

S. N. ROY, Lucknow.

It is submitted that in (1) the process of titration, (2) Raoult's Law (3) Suction through semi-permeable membranes, (4) Avogadro's law, (5) Dulong and Petit's law, (6) Wiedemann Franz law, (7) Faraday's laws of electrolysis, (8) Aston's isotopes, (9) the so-called "electron" all the phenomena are capable of explanation without assuming that atoms have necessarily either the same mass or size and by assuming only that an element is settled by its value of the Faraday ratio  $e/m$ .

15. Adsorption at liquid interfaces.

P. B. GANGULY *and* D. N. GHOSH, Patna.

An apparatus has been set up with a view to study the applicability of Gibb's adsorption equation to a liquid system. It consists of an arrangement in which the freshly formed drops of liquid paraffin are exposed to a column of a solution whence they are collected in to a separate vessel along with thin films of this solution with which they are surrounded. The small changes in the concentration of these solutions have been measured by means of an interferometer.

Adsorption of electrolyte solutions like silver nitrate, potassium chloride, sodium chloride and also of non-electrolytes like solutions of caffeine, cane sugar, etc., have been measured in this way and the results have been discussed in the light of Gibb's adsorption equation.

16. Adsorption of soaps on the surfaces of copper and nickel. (A preliminary study.)

B. S. SRIKANTAN *and* A. S. MENON, Bangalore.

In order to account for the preferential hydrogenation of the more unsaturated glycerides usually met with in the hydrogenation of oils, a preliminary study of the adsorption of soaps on the surfaces of nickel and copper at  $30^\circ\text{C}$ . was undertaken. The applicability of Freundlich's equation is considered.



### 17. Anomalous adsorption of ions by the arsenious sulphide sol in the presence of protecting agents.

S. S. JOSHI and A. JOGA RAO, Benares.

Ionic adsorption from different electrolyte solutions by the  $\text{As}_2\text{S}_3$  sol treated with an equal volume of solutions of different protecting agents has been studied. In any series of experiments, the volume of the sol, its colloid content, the volume, the concentration of the electrolyte solution, and the total volume were kept constant. It was found that the ionic adsorption by the colloid protected initially by varying amounts of the protecting agent showed maxima and minima on the adsorption—protector concentration curve. This anomaly was observed only when dilute solutions of the protector were employed; with concentrated solutions of the latter the adsorption was normal, that is, it increased continuously as the concentration of the protecting solution was increased. This last was also observed when no protector was used, and the adsorption due to increasing amounts of the colloid from a constant amount of the electrolyte solution was measured.

### 18. On adsorption by active charcoal.

S. ROYCHOUDHURY, Calcutta.

The adsorption of electrolytes and the charge carried by charcoal prepared from sugar and gelatine and activated at different temperatures and with several gases have been measured. Similar experiments have also been carried out with purified and activated charcoal obtained from Merck's animal and blood charcoal. The work is in part repetition of previous works and refers to the difference of opinion existing in the literature on (a) 'molecular adsorption of salts and acids' as opposed to adsorption of ions (b) the charge carried by different samples of charcoal, (c) relative adsorbability of alkali and acid with reference to hydrolytic adsorption of salts, and (d) the conditions of activation. The broad results are (i) the adsorption of ions takes place, (ii) the charge is related to the adsorption properties, and (iii) that under different conditions of activation quantities of other substances are produced which affect materially the charge.

### 19. Adsorption and heats of adsorption.

J. G. KANE.

In continuation of previous work, animal charcoal treated with hydrofluoric acid to remove ash and activated in the usual way has been found to give, when brought into contact with mixtures of toluene and acetic acid in different proportions, an adsorption isotherm the reverse of that obtained with sugar charcoal, indicating that the latter preferentially absorbs toluene and the former acetic acid.

The heats of adsorption of the same mixtures by activated silica, animal charcoal and sugar charcoal have been determined using the method of twin calorimeters. The relation between the excess of heat observed over that calculated from the heat of wetting of the components and the composition of the binary mixture is of the same nature as the adsorption isotherm.

### 20. A note on adsorption.

A. GANGULI, Benares.

In a recent publication Kar and Ganguli derived statistically Langmuir's well-known equation of adsorption and obtained for the Langmuir Constant  $K$

$$K = \frac{(2\pi mkT)^{\frac{1}{2}}}{h} e^{-\frac{a}{kT}} \quad . \quad . \quad . \quad . \quad . \quad (1),$$



Where  $h$  is Planck's constant and 'a' the adsorption potential. Sometime back, Fr nkel derived Langmuir's formula from the classical kinetic theory

$$\frac{n}{s} = \frac{n'}{V} \tau_0 \sqrt{\frac{kT}{2\pi m}} e^{\frac{u_0}{kT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Where  $u_0$  is the heat of adsorption,  $n'$  the number of particles striking the surface,  $n$  is the number of molecules adsorbed,  $s$  the surface of the adsorbent and  $\tau_0$  the period of oscillation of the adsorbed molecule. In this paper it is shown that making area correction corresponding to van der Waal's 'b' correction, identifying  $u_0$  with 'a' in equation (1) and again assuming  $h\nu = kT$  (where  $\tau_0 = \frac{1}{\nu}$ ) we obtain the same value of 'K' as in equation (1). It is interesting to note that the statistical formul e of Sexl and of H ckel can also be converted into the said formula of Kar and Ganguli if the assumption is made that  $h\nu = kT$ , and 'a' identified with the potential energy  $\chi$  of the molecule in the gaseous state (Sexl) and the adsorption potential  $\epsilon$  of H ckel. It may be further mentioned that if  $\frac{h}{\tau_0} = kT$ , we obtain the value of  $\tau_0$  of the order of  $10^{-13}$  Sec. in agreement with the experimental value.

## 21. Heat of wetting of silica gel.

R. C. RAY and P. B. GANGULY, Patna.

An activated sample of silica gel of known water content was exposed to water vapour at different pressures, and the amount of water adsorbed at each pressure was estimated. In this manner, silica gels of different and known water content were obtained. The heat of wetting of these gels has been measured, and the relationship between the quantity of water in the gel and its heat of wetting has been determined.

## 22. Studies on the effect of ultra-violet light on colloids. Part—IV.

PANNA LAL and P. B. GANGULY, Patna.

In continuation of previous papers (*J.I.C.S.*, 1929, 1930), the coagulation of sulphur sol, of Carey Lea's silver sol, and of silicic acid sol have been studied in detail. The effect of light on Wackenroder's solution, on thionic acids and on ferrous citrate have been investigated and it has been found that the coagulation of colloidal solutions, where the above named electrolytes act as stabilisers, can be explained on the basis of the photochemical changes brought about in the stabilisers themselves.

## 23. Effect of dilution and purity of a colloid on the coagulating values of different electrolytes.

P. M. BARVE, Bombay.

The effect of dilution of colloids on electrolyte concentration required for coagulation, has been recognised for a long time. In a series of papers, Dhar and others have studied the effect of the changes in the concentrations of different sols on the coagulating values of different electrolytes. From the results, they have formulated a general dilution law which states that with increasing dilution of a colloid, the amount of an electrolyte required for coagulation becomes less, provided the sol does not appreciably adsorb from the coagulating electrolyte the ions carrying the same charge as the colloid.



With a view to test the validity of the above generalisation experiments on the coagulation of thorium hydroxide sol, of different concentrations, and dialysed for different periods, were carried out. The electrolytes chosen were KCl,  $K_2SO_4$ ,  $MgCl_2$ ,  $MgSO_4$ ,  $AlCl_3$ ,  $Al_2(SO_4)_3$ .

The general dilution law is followed only qualitatively. But in the case of  $AlCl_3$  a greater amount of electrolyte is required to coagulate a dilute sol than that required for a concentrated sol.

On dialysing the sol it was observed that the ratio of the quantities of electrolyte required for coagulating the sol at two different stages of dialysis, changed considerably with different electrolytes.

These results incline one to believe that there is adsorption of similarly charged ions in every case.

## 24. Studies in the hydrolysis of gelatine.

G. M. NABAR, Bombay.

The protecting influence of hydrolysed gelatine on the precipitation of silver chromate from aqueous mixtures of silver nitrate and potassium chromate has been studied electrometrically.

It is found that in the beginning, the *e. m. f.* of the system remains constant as long as the precipitate does not appear; it then falls slowly through a small range and finally remains constant.

The activity of silver ion has been calculated from the *e. m. f.* data for different stages of precipitation.

The results show that the efficiency of gelatine for keeping the silver chromate in supersaturated conditions increases with progress of hydrolysis.

The results are discussed from the point of view of existing data on the subject.

## 25. The scattering of light in protein solutions and gels. I. Gelatin.

K. KRISHNA MURTI, Nagpur.

The variation of the intensity and depolarisation of the scattered light with temperature and concentration of gelatin sols and gels has been examined. Gelatin sols above  $30^\circ$  have been considered to be polydisperse systems, in which part of the gelatin is present in the molecularly dispersed conditions and the rest as polymolecular micelles. Cooling a sol (at pH 4.8) below  $25^\circ$  produces supersaturation as a result of which condensation of molecular gelatin into aggregates takes place. An ultracentrifugal examination of gelatin sols at pH 4.8 shows clearly that considerable aggregation of gelatin molecules takes place at about  $20^\circ$ . This is also supported by an ultramicroscopic examination.

During gel-sol transformation the gel micelles are gradually dispersed into the original molecular condition.

The molecular state of gelatin in the sol is discussed.

When gelatin sols of pH 4.8 are cooled below  $25^\circ$  the depolarisation of the scattered light first decreases and then increases; and this effect is more pronounced in the case of dilute sols. The significance of these effects in revealing the changes in size and shape of the micelles is pointed out.

## 26. The structure of gelatin gels.

K. KRISHNA MURTI, Nagpur.

An ultramicroscopic examination of gelatin gels (pH 4.8) shows that: (a) the gels are polydisperse systems, (b) the particles are nearly spherical in shape, (c) they are separated from one another by distances of



the same order of magnitude as the diameter of the particles, (d) the gel particles sometimes form a kind of net-work, or, as is more often the case, they arrange themselves in parallel rows.

Gelatin sols of about 2% concentration or more (pH 3) set to gels without any change of light scattering, showing thereby that aggregation of the particles is not an essential condition for the formation of gels. It is therefore probable that the capacity of the particles to "bind" water is the main factor responsible for the formation of gels. Only a part of the water contained in the gels is actually bound by the gel particles. Further, the particles are not in actual contact, but are separated by thin films of water. The author puts forward a view of gel structure to bring all the facts into harmony.

## 27. The scattering of light in silicic acid sols. Part I— Mechanism of the formation of colloidal particles.

K. KRISHNA MURTI, Nagpur.

The formation of silicic acid sol by the surface condensation and also volume condensation processes has been followed by means of light scattering measurements.

In the surface condensation process the time-Tyndall number curves show a rapid increase of the intensity with time at first, and after some time there is a bend in the curves. The conclusion reached after a careful examination of the results is that, at first, extremely fine colloidal particles are formed, and that these form aggregates later on.

In the *volume condensation process* the time-Tyndall number curves are first more or less straight, but later on they are curved concave to the time axis. It is suggested that primary particles are formed at first, but after a time the molecular silicic acid formed in the reaction condenses on the particles leading to the formation of larger particles.

## 28. The scattering of light in silicic acid sols. Part II— Ageing of the sols and their gel formation.

K. KRISHNA MURTI, Nagpur.

The changes in the intensity and depolarisation of the scattered light during the ageing of silicic acid sols have been studied. On plotting the results we get a time-Tyndall number curve which is S-shaped. The analogy between ageing and slow coagulation is pointed out, and a mathematical expression is derived which is found to be in good agreement with the results obtained.

The viscosity of the sol increases during ageing and finally the sol sets to a gel. No abrupt changes in light scattering were observed during gelation.

## 29. Derivation of Planck's radiation law from the point of view of adsorption.

A. GANGULI, Benares.

In a series of papers equations for chemical and electrical adsorption were derived by the application of Gibbs's Statistics. Later on the same idea was extended to the adsorption of electrons, thus leading to Saha and Richardson Equation. In the present paper the generalised Gibbs Statistics in the form of Bose—Einstein is applied to the case of adsorption of radiation quanta. An equilibrium between the free quanta and the bound (or adsorbed) quanta led to the well-known radiation law. By



taking into consideration the effect of the quanta already adsorbed on the phase volume of the number of quanta in the bound state, the following modified form of Planck's radiation law is obtained :

$$u_{\nu} d\nu = \frac{8\pi h\nu^3 d\nu}{c^3 \left( e^{\frac{h\nu}{kT}} - 1 \right)} + \frac{(8\pi)^2 h\nu^5 / T^3 \cdot \beta d\nu}{c^6 \left( e^{\frac{h\nu}{kT}} - 1 \right)^2}.$$

Where  $\beta$  is a constant, and the other symbols have the usual significance. The correction term is similar to that of Strum but differs by the factor  $h\nu$ , since we have taken the proportional correction factor to the number of quanta and not to the radiation density. The correction term, however, is negligible for all practical purposes since it contains the term  $(d\nu)^2$ .

### 30. The 'wall effect' in colloid reactions.

S. S. JOSHI and V. L. NARAYAN, Benares.

It is known that an overwhelming majority of changes in the gaseous medii are influenced markedly by the wall catalysis in the reaction vessel. Since surface reactivity is the chief factor in almost every phase of colloid behaviour, it is extremely interesting to investigate the possibility of the 'wall effect' in colloid changes. That the walls of the containing vessel can be anything but an inert constituent of the colloid system, was indicated by results (shortly to be published) observed in these Laboratories, namely, that the autocoagulability of a sol can be considerably modified by charging the walls of the containing vessel to a suitable potential. With uncharged surfaces it was found that the different colloids did not behave in the same way. Thus, for instance, in the case of the  $\text{As}_2\text{S}_3$  sol it was observed as a result of numerous experiments that its coagulation over a wide variation of the wall (glass) surface, corresponding to an approximately constant volume of the reacting mixture, was entirely unchanged. The same result was observed when the surface was carefully paraffinated. An example of the opposite type was found in the coagulation of the  $\text{MnO}_2$  sol, in which a definite increase in the coagulation rate was observed by increasing the wall (glass) area; paraffinating the latter had opposite effect.

### 31. Variation of viscosity during the coagulation of the arsenious sulphide sol.

S. S. JOSHI and P. V. RATNAM, Benares.

It was observed that the viscosity of the coagulating sol diminished to a minimum in the early stages of coagulation and then increased. This is discussed from the standpoint of the variation during coagulation of the (i) charge, (ii) the state of hydration, and (iii) the size of the colloid particles. In the region of slow coagulation the viscosity increased in accordance with the equation for a monomolecular reaction. With a much greater coagulator concentration, however, the monomolecular constant decreased continuously during the progress of coagulation. This indicates that the corresponding order of the reaction involved in the observed viscosity variation is less than unity. This conflicts with Smoluchowski's theory unless, even approximately, the viscosity variation is not a measure of coagulation for all values of electrolyte concentrations, as is usually assumed to be the case.



32. Viscosity measurements of certain sols in presence of electrolytes and the study of the change of viscosity and conductivity on ageing.

D. N. CHAKRAVARTI, Amraoti, (Berar).

The viscosity measurements of the following sols in presence of electrolytes have been carried out by Farrow's method (1) chromium arsenate, (2) ferric borate, (3) ferric phosphate, (4) cerium borate, (5) Cerium molybdate, and (6) zirconium borate. In all these cases there is a decrease in viscosity when small quantities of electrolytes are added and then an increase with the increasing concentration of the electrolyte till the coagulation point is reached. The decrease in viscosity is ascribed to the increase of charge on the sol by the adsorption of ions carrying the same charge as the sol. The increase of charge on the sol is also associated with the decrease in hydration and with it the viscosity. But when increasing quantities of electrolytes are added the adsorption of ions carrying opposite charge is more than the adsorption of ions carrying the same charge as the sol and so there will be an increase in hydration and consequently the viscosity increases till the coagulation point is reached.

The effect of viscosity and conductivity on ageing is studied in order to classify the sols into hydrophobe and hydrophile colloids according to our rule that for hydrophobe colloids the viscosity decreases and conductivity increases and for hydrophile the viscosity increases and conductivity decreases.

33. Effect of the concentration on the viscosities of vanadium pentoxide sols of different degree of purity.

C. AHOBALACHARYA and S. GHOSH, Allahabad.

Viscosities of vanadium pentoxide of different purity were determined for various concentrations of the sols. In the determination Ostwald's viscometer was used. It is found that the concentration viscosities curves are not straight lines showing that the Einstein's equation is not applicable to this sol. The equation of Hess gives a curve for the graph of the viscosity concentration. Accordingly this equation was applied to the experimental results of vanadium pentoxide sols and it is found that the value of "effective volume" or the hydration for one gram of colloid markedly varies and is not constant. The value is irregular, it is neither of the increasing or decreasing order as the concentrations of vanadium pentoxide sols are increased. Hatschek's formula for emulsions was not applied as the maximum concentration of vanadium pentoxide sol under investigation was less than 1.5%.

As the process of dialysis continues, the vanadium pentoxide sols are obtained of different purity and it is observed that the curve becomes more and more steep with the purity of the sol. The dilute sol (0.1%) shows little change of viscosity with the increasing purity and this change becomes more and more marked as the concentrations of the vanadium pentoxide sols are increased. Thus 0.1% sol of vanadium pentoxide after 24 hours of dialysis recorded a viscosity of 0.00841 and after 144 hours of dialysis the value increases to 0.00865; whilst 1.4% sol of vanadium pentoxide after 24 hours of dialysis gives a viscosity of 0.021 and after 144 hours of dialysis the sol becomes more than 10 times as viscous.

The authors venture to suggest that the increase in the viscosity of vanadium pentoxide sols with purity is slightly due to the increased hydration of the colloid particles and this is indicated by the increase in the viscosity of the diluted sols. The high percentage of increase in the viscosity of concentrated vanadium pentoxide sols with purity is probably due to some structure which the colloid particles assume as the electric charge on the colloid particles decreases. It is obvious that the chances of



the formation of a structure is more in a concentrated sol than in a diluted one.

### 34. Viscosity of agar sol.

S. N. BANERJEE and S. GHOSH, Allahabad.

The viscosities of agar sols of various concentrations have been determined at different temperatures using Ostwald's viscometer and the following results are obtained :—

- (1) The curve for the viscosity-concentration is not a straight line.
- (2) As the temperature is increased the curve is flattened out and becomes less and less steep.
- (3) The temperature coefficient of the viscosity increases rapidly with the fall in temperature. The increase is most rapid with dilute sols of agar.
- (4) The greater the concentration of the agar sol the greater is the temperature coefficient of the viscosity.
- (5) The increase of the viscosity with time is very slow. No change in the viscosity is observed within half an hour at temperatures  $10^{\circ}$  above the gelation temperature. Near the gelation temperature slight increase in the viscosity is observed within 30 minutes.
- (6) Rapid increase in the viscosity of agar sol occurs when the sol is sown with already formed gel. Within 30 minutes the sol becomes twice as viscous.
- (7) The phenomenon of hysteresis in the sol-gel transformation or the difference in the melting and settling points for agar sols is highly developed. This has been ascribed (cf. Banerjee and Ghosh. *Zeit. Anorg. Chem.* 1930) to the slow velocity with which the aggregates of colloidal agar particles appear with time to form gel. This view is supported by the fact that the increase of viscosity of agar sols with age is extremely slow.
- (8) The experimental results of this paper have been explained on the view that in agar sols, specially near the gelation temperature the colloid particles assume a structure to arrange themselves in a certain form.
- (9) It is suggested that the force which causes this arrangement originates from "a loose crystallographic force". The appearance of gel from a sol in the sol-gel transformation resembles the separation of solid from a supersaturated solution.

### 35. Potassium chromate and potassium dichromate as light filters and the constitution of chromic acid from absorption measurements.

W. V. BHAGWAT and N. R. DHAR, Allahabad.

The absorption and percentage transmission in the visible region for aqueous solutions of various concentrations of potassium chromate and potassium dichromate have been determined. It is shown that a saturated solution of potassium chromate transmits all wavelengths longer than  $5150 \text{ \AA}$  while potassium dichromate can conveniently be used to cut off all wavelengths shorter than  $5600 \text{ \AA}$ . It is observed that combination of cobalt glass with a saturated solution of potassium dichromate or chromate transmits only infra-red.

In very dilute solution chromate and dichromate of potassium behave markedly similar to each other and hence chromic acid in dilute solutions appears to exist mainly as  $\text{H}_2\text{CrO}_4$ .



## 36. Copper salts as light filters.

W. V. BHAGWAT and N. R. DHAR, Allahabad.

The use of copper salts as light filter has been thoroughly investigated. Various concentrations of the aqueous solutions of the salts have been employed and their extinction coefficient, absorption, and percentage transmission in various regions of the visible spectrum have been determined. It is observed that with increasing dilution the different salts behave similarly indicating complete ionisation and hence the similar effect is attributed to cupric ions. In concentrated solutions it is the effect of undissociated molecules especially with cupric chloride where the colour is not blue but green. A saturated solution of cupric chloride transmits only 5066 to 5800 Å, while a saturated solution of cupric nitrate cuts off all wavelengths longer than 5732 Å and a saturated solution of copper sulphate transmits all region shorter than 6500 Å.

## 37. Absorption and extinction coefficient of crystal violet, methyl-violet and methylene blue.

W. V. BHAGWAT, Allahabad.

It is observed that methyl violet absorbs from 6500 Å. to 5000 Å. of the visible spectrum. Crystal violet absorbs a shorter range extending from 6300 Å. to 5200 Å. and range of absorption for methylene blue extends over all the wavelengths longer than 5466 Å. The respective concentrations are 0.10 grs., 0.008 grs., and 0.0232 grs. per 100 c.c. The use of these substances as solution filters has been discussed. It is observed that for same range of transmission methyl violet is better than crystal violet as it has got higher percentage of transmission. The absorption and percentage transmission at various concentrations of the same substances have also been determined.

## 38. Mixture of two solutions as solution filters.

W. V. BHAGWAT, Allahabad.

In search of suitable light filters various mixtures of solutions have been studied. Thus the combinations of copper chloride and potassium chromate, copper chloride and potassium dichromate, copper chloride and methylene blue, methyl violet and potassium dichromate, copper nitrate and potassium dichromate are investigated. In all the cases a thorough knowledge has been obtained by varying the concentrations of both the constituents of the mixture. These combinations offer a very short range of transmission, thus giving us a definite wavelength to study its photo-chemical effect. The combination of potassium dichromate and methyl violet or crystal violet is very suitable for red region, while its combination with copper chloride transmits only green.

## 39. Kinetics of coagulation from the standpoint of Smoluchowski's theory. Part I. Antimony sulphide sol.

S. S. JOSHI and S. M. PRABHU, Benares.

A review of the literature on the subject showed that the above theory has been examined chiefly with respect to the equation,

$$n_t = \frac{n_0}{1 + \beta t}, \quad (i)$$

where  $n_0$  and  $t$  denote respectively the original number of particles called the primaries and the velocity constant.  $n_t$  gives the total number of



particles in all stages of coalescence at a time  $t$ . In the present work  $\beta$  was evaluated from general results in Smoluchowski's theory, *viz.*,

$$\beta = \frac{1}{t} \left[ \sqrt{\frac{n_0}{n_1}} - 1 \right] \quad (\text{ii})$$

where  $n_1$  denotes the number of primaries at a time  $t$ .  $n_1$  was evaluated by an analytical determination of the unprecipitated colloid content in a given volume of the coagulating sol within a given time. It was found that contrary to the requirements of Smoluchowski's theory the velocity constant increased to a maximum during the early stages of coagulation and then diminished. The coagulation rate was found to increase markedly by increasing the temperature. Values of  $\beta$  during the early stages of coagulation at different temperatures were found to be approximately equal to those deduced from Smoluchowski's equation.

#### 40. Kinetics of coagulation from the standpoint of Smoluchowski's theory. Part II. Arsenious sulphide.

S. S. JOSHI and S. M. PRABHU, Benares.

Applying the method of measuring the coagulation rate followed in Part I, it was found that the coagulation of the  $\text{As}_2\text{S}_3$  sol in some ways differed markedly from that of the  $\text{Sb}_2\text{S}_3$  sol. The value of  $\beta$  evaluated from equation (ii) in Part I in coagulations due to different electrolyte concentrations, diminished continuously during the coagulation time, the diminution being more marked greater the dilution of the coagulator solution. The increase of  $\beta$  observed during the early stages of the coagulation of  $\text{Sb}_2\text{S}_3$  in Part I was not noticed. In the region of slow coagulation, within a limited range of the coagulator concentration, results were found to be in approximate agreement with the equation of Paine (*Kolloidchem. Beih.* 1912, 4, 24) and of that for the autocatalytic reactions employed by Gann and others (*ibid.*, 1916, 8, 65).

The influence of temperature on the coagulation rate using sols of different colloid contents, has been studied in the temperature range 12–70°C and was found to be much less pronounced than that observed in the case of  $\text{Sb}_2\text{S}_3$  sol. The values of  $\beta$  observed at different temperatures in the above range were found to be smaller than those deduced from Smoluchowski's theory, the discrepancy being greater the higher the temperature of the coagulating system.

The temperature effect has also been investigated on coagulations produced in the presence of different sensitising and protecting agents, with a view to examine if their rôle in the micellar processes to any extent resembles the positive and negative catalysis in molecular chemical reactions.

#### 41. The Kinetics of coagulation from the standpoint of Smoluchowski's theory. Part III. Variation of the refractive index during coagulation.

S. S. JOSHI and G. R. GODBOLE, Benares.

A study has been made of the values for the refractive index,  $\mu_D$  of the  $\text{As}_2\text{S}_3$  sol under different conditions of temperature, colloid content, and coagulated by different electrolyte solutions of various concentrations. It was found that  $\mu_D$  increased continuously during coagulation and measurements were taken until when the turbidity of the coagulating system became too great to let any light through, or when a steady state was reached in which no further change in  $\mu_D$  occurred. It was observed that the value of  $\mu_D$  characteristic of this steady state diminished as the coagulator concentration was reduced. A precisely similar effect was



noticed in sols of varying colloid content, coagulated by an electrolyte solution of constant concentration. In different series of experiments in which the colloid content of the sol was varied and the coagulator concentration kept fixed, in agreement with Smoluckowski's theory the relative times corresponding to a given value of  $\mu D$  were constant. This agreement was less marked in the other series in which different coagulators of various concentrations were employed to coagulate a sol of constant colloid content.

42. Influence of purity and temperature on the ratio of the precipitating values of mono- and bivalent cations with vanadium pentoxide sols.

C. AHOBALACHARYA and N. R. DHAR, Allahabad.

The ratio of the precipitating concentrations of uni- and bivalent ions has been measured with a sol of vanadium pentoxide at different stages of dialysis at ordinary temperature. It is found that the ratio continuously diminishes as the process of dialysis is continued and the sol becomes more and more purified. This result confirms the deductions of Chakravarti, Ghosh, and Dhar. (Jour. Phy. Chem. 1930, 34, 326), that as the electric charge on a colloid particle decreases the precipitating concentrations of uni-, bi-, and trivalent ions have a tendency to approach the value of  $1 : \frac{1}{2} : \frac{1}{3}$ .

That the electric charge on the colloid particles decreases in the course of dialysis is further supported by the fact that the viscosity increases with the purity of the sols. (Cf. Dhar, Ghosh. Koll-Zeit, 1929, 48 (1), 43).

Effect of temperature on the precipitating concentrations of uni- and bivalent ions were also investigated with this sol, and it was found that the ratio of the precipitating concentrations increases with the increasing temperature showing that the electric charge on the colloid particles of vanadium pentoxide increases with the heating of the sol. Ghosh and Dhar have shown that some vanadium pentoxide is present as simple and complex vanadic acid molecules in a vanadium pentoxide solution and with the increasing temperature the dissolved material increases in amount. It is probable that at high temperatures the presence of greater amounts of vanadic acid in the dissolved and solution state is responsible for increasing the electric charge on the colloid particles.

43. Kinetics and energetics of the hydrolysis of cane sugar.

A. K. BHATTACHARYA, Allahabad.

The kinetics of the hydrolysis of cane sugar have been investigated in light of different wavelengths using various solution filters and at different temperatures in each wave region. The energetics of the same reaction have also been determined.

It is found that the reaction is not only accelerated by tropical sunlight but also in various wavelengths of the visible spectrum using 1000 watt gas filled tungsten filament lamp as a source of light. The reaction is accelerated even by wavelengths very near to critical wavelength calculated according to the modified radiation hypothesis.

44. Kinetics, temperature coefficients, and quantum efficiency of some photo-chemical reactions in different wave-lengths.

K. N. MALAVIYA and N. R. DHAR, Allahabad.

We have studied the reaction of bromine on propyl, isopropyl, and normal butyl alcohols in wave-lengths 8500 Å., 6800 Å., and 5660 Å. All



these reactions proceed with measureable speed in the dark and the light acts as an accelerator only. There is appreciable acceleration in all the regions, the maximum being in 6800 Å. where transmission is 60% and least in 5660 Å. where the transmission is only 0.9%. This clearly shows that intensity of light also accounts for much in photo-chemical reactions.

The temperature coefficients of purely light reactions have been obtained by subtracting the velocity of the purely thermal reaction from the total velocity obtained by exposure to light. The temperature coefficients are greater than unity.

All these reactions are unimolecular with respect to bromine and Einstein's law of photo-chemical equivalence is not obeyed. The quantum efficiency increases with rise in temperature.

The velocity of these reactions is nearly proportional to the intensity of the incident light. On the other hand by adding KBr, *i.e.*, by decreasing the velocity of dark reaction, the effect is that the velocity varies almost as the square root of the intensity.

#### 45. Variation in extinction coefficients during the course of jelly formation.

SATYA PRAKASH and N. R. DHAR, Allahabad.

1. The variations in extinction coefficients during the process of gelation of various hydroxide, arsenate, phosphate, molybdate, and borate jellies have been investigated and the percentage of light transmitted at different intervals has been calculated.

2. According to these results, the jellies have been divided into three groups: (1) Perfectly transparent jellies, showing no variation in extinction coefficients either during the process of gelation or after the setting of the jelly. (2) The jellies, opalescent at the point of setting and transmitting only a portion of light but the opacity increasing with time and finally, in some cases, becoming perfectly opaque. (3) The jellies obtained from clear sols, but becoming opaque before or at the point of setting.

3. Where the opacity increases even after the setting of jellies, it has been observed, that the extinction coefficients vary continuously and there is no marked break in the curve at the point of setting.

4. The transparency and opacity of the jellies have been explained on the basis of the authors' hypothesis of the agglomeration and hydration tendencies of the jelly-forming particles.

5. With the sols of zirconium molybdate and borate, it has been shown that when they are coagulated by chloride ions, the jellies are opalescent but when by sulphate ions, the jellies are transparent.

6. The impure sols yield comparatively opaque jellies because in that case, the agglomeration tendency of the particles is more favoured. The greater the purity of the sol, the greater will be the hydration tendency of the particles.

#### 46. Influence of temperature on the setting of jellies.

SATYA PRAKASH, Allahabad.

1. The influence of temperature on the time of setting of various jellies has been investigated.

2. According to the influence of temperature, the jellies can be divided into two groups. The inorganic jellies which take less time to set at higher temperatures, as zirconium hydroxide, zirconium molybdate, zirconium borate, thorium phosphate, thorium molybdate, and zinc arsenate. The jellies of vanadium pentoxide, thorium arsenate and mercurisulphosalicylic acid appear to be exceptional. These jellies do not set at all above a certain temperature (60°-70°).



3. The organic jellies of gelatin, agar agar, starch soaps, etc., belong to the second group and their gelation is favoured by a low temperature.

4. The temperature influence on the setting of jellies is guided by the solubility, hydration and hydrolysis of the dispersed phase, and the rate of the formation of colloidal phases where the jellies are obtained by the metathetical reactions, and the rate of coagulation at higher temperatures.

47. The relation between coagulation and gelation points of jelly forming sols and the formation of jellies by ageing.

SATYA PRAKASH, Allahabad.

1. As no work on the coagulation of such jelly forming sols as ferric arsenate, chromic arsenate, various phosphates, molybdates, etc., has been done as yet, an investigation in this direction has been undertaken.

2. It has been shown that the sols of ferric arsenate, ferric phosphate, etc., are positively charged and not negative as Holmes thinks.

3. From coagulation and gelation experiments on ferric arsenate, chromic arsenate, zirconium borate, zirconium molybdate and titanate acid sols, it has been shown that the coagulation and gelation points of these sols are quite distinct and more electrolyte is necessary to give a jelly than to coagulate the sol in the same time.

4. With the dialysed sols of ferric phosphate, ferric tungstate, stannic borate, ceric borate, and chromic arsenate, it has been shown that when sufficiently purified by dialysis, they set to jellies by themselves on ageing without the addition of any further coagulating electrolytes. Subsequently, some of these jellies begin to synerise also.

5. These results on the ageing of sols and jellies are interesting from the view point that they offer an explanation to the spontaneous clotting and subsequent syneresis of blood, the only difference being that in case of blood, the process is more rapid.

48. On the existence of a critical coagulation potential.

M. M. BISWAS and J. MUKHERJEE, Calcutta.

A review of recent measurements of the cataphoretic speed of colloidal particles showing that one of the authors' contention (J.N.M.) that no such critical potential exists is firmly established on facts. Results of further experiments (by M. M. Biswas and S. Gohain Rajkumar) are reported corroborating the above. They also support the other contention that there is little or no parallelism between the original cataphoretic speed of the colloid and that at the coagulating concentration.

49. On the concept of "colloidal acids".

H. K. Sen and J. MUKHERJEE, Calcutta.

A large number of measurements on the titration (*e.m.f.* and conductometric) of insoluble or sparingly soluble acids and bases in colloidal and saturated solutions as also in a state of coarse suspensions has been made. The results bring out clearly (i) a 'time' effect, (ii) the rôle of interfaces, and (iii) the effect of displacement of adsorption equilibrium of small traces of electrolytes present in the system. The results are discussed in relation to the theories advanced to explain the acid properties of clay. It is shown that a characteristic orientation based on the phase rule is possible which is free from the defects of older theories.



### 50. Measurements of the activity of hydrogen ions in various mixtures of phosphoric acid with neutral salts.

S. K. MAJUMDAR, Calcutta.

The activities are calculated from *e.m.f.* measurements and have the usual limitations. Parallel experiments with indicators have been made. The relative variations in activities may be taken to be sufficiently accurate for the purposes of the theoretical discussion. Departures from the Debye-Hückel theory are pointed out.

### 51. Theories of Liesegang rings and periodic precipitation.

A. C. CHATTERJI, Lucknow.

In this paper it has been shown that there is not sufficient experimental evidence for Bradford (*Journ. Soc. Chem. Industry*, 1929, 48. 78) to assume that the adsorption of ions plays an important part in Liesegang ring formation.

Direct experiments on the adsorption of chromate ions by lead chromate precipitate freshly formed, have been undertaken and it has been observed that the adsorption of the chromate ions is very little. Whereas, in contrast to this, the adsorption of lead chromate sol, either stabilised by gelatine or agar-agar by lead chromate precipitate is considerably greater.

Therefore, if adsorption is responsible for the production of clear spaces in Liesegang rings, then the adsorption of the sparingly soluble substances in the peptised condition is more effective and not the adsorption of either of the reacting substances in the ionic state as is supposed by Bradford.

The above observation is in accord with our theory which introduces two new conceptions in the phenomenon of periodic precipitation.

(1) The sparingly soluble substances formed exist at first in the colloidal state in presence of the gel.

(2) The solid precipitates can adsorb and coagulate the same substance existing in the colloidal state in the gel or medium.

Numerous experiments carried out in various directions support our theory.

### 52. Studies on the formation of Liesegang rings.—VII.

L. N. MUKERJI and A. C. CHATTERJI, Lucknow.

Exhaustive studies on the formation of Liesegang rings in the following inorganic gels have been carried out:—

Ferric molybdate, stannic arsenate, thorium arsenate and thorium phosphate.

Attempts have been made to produce rings of the following substances with the above jellies:—

Chromates of lead, barium and silver; sulphates of barium, strontium, and lead; ferricyanides of silver barium, lead, cobalt, nickel, copper and manganese; and cyanides of copper, nickel, cobalt and manganese.

Rings were obtained in stannic arsenate jelly with the following substances:—

(1) Ferricyanides of cobalt, copper and manganese. •

Rings were obtained in thorium arsenate jelly with the following substances:—

(2) Ferricyanides of silver, manganese, copper, and nickel.

The effects of the change in the concentration of the reacting electrolytes and of the gel have been also investigated and it has been found that a change in the concentration of the diffusing electrolyte is as effective on ring formation as a change of the solute in the gel.



53. Chemiluminescence in the oxidation of dihydric and trihydric phenols by ozone and hydrogen peroxide.

N. N. BISWAS, Allahabad.

When dihydric and trihydric phenols are oxidised by ozonised oxygen a glow, which is visible in the dark room, is observed.

When dihydric and trihydric phenols such as catechol, resorcinol, quinol, pyrogallol, hydroxyquinol are oxidised by hydrogen peroxide and ferrous sulphate a glow is observed in a dark room.

The influence of solvents on the intensity of the glow has been studied. In amyl alcohol good glow is observed but the glow lasts only for a short time when a rapid stream of ozonised oxygen is passed.

Increase of temperature of the reacting substances leads to the intensification of the glow.

Increase of concentration of the reducing agents causes an increase of the intensity of the glow up to a limiting value; if the concentration is increased further the glow becomes less.

54. The radiation hypothesis of chemical reactions.

G. GOPALA RAO and N. R. DHAR, Allahabad.

One of us has put forward the view that the wave-length obtained by calculation from the temperature coefficient of a reaction represents the threshold limit. Radiations of wave-length shorter than the threshold limit accelerate the reaction provided they are absorbed, and radiations of wave-length longer than the threshold limit are without influence. According to this new conception, the reaction proceeds under the influence of light of the calculated wave-length with the minimum speed.

It has been found that the quantum yield in various photochemical reactions increases with decrease in the wave-length of the radiation. We have now plotted the quantum yield against wave-length for the following reactions:—

- (1) Inversion of cane sugar.
- (2) Decomposition of sodium cobaltinitrite.
- (3) The reaction between potassium oxalate and bromine.
- (4) The oxidation of citric acid by chromic acid.

A smooth curve is obtained in each case; and by extrapolation to zero quantum yield we have obtained the threshold wave-length under the influence of which there should be no reaction. The threshold limit thus obtained agrees fairly well with that calculated from the temperature coefficient of the dark reaction using the Marcelin-Rice formula. This fact lends great support to the modified form of the radiation hypothesis.

55. Photo-sensitised oxidation of ammonia and ammonium salts and the problem of nitrification in soils.

G. GOPALA RAO, Allahabad.

We have found that ammonia and ammonium salts in aqueous solution are appreciably oxidised to nitrite in the presence of sunlight and various photo-sensitisers like titanium dioxide, zinc oxide, cadmium oxide, alumina and silica. Titania is the most and silica is the least active in this respect. The oxidation is unaffected by the accumulation of the reaction product, namely, nitrite. The pH of the solution has a profound influence on the reaction velocity, alkalinity increases and acidity diminishes the rate.

These experiments on the photo-sensitised oxidation of ammonia and its salts seem to throw new light on the mechanism of nitrification in the



soil. We suggest that nitrification can take place in the absence of bacteria provided sunlight is present. The nitrification takes place at the surface of various oxides present in the soil which absorb light energy. This photochemical theory of nitrification explains many known facts which cannot be made to fit in with the bacterial hypothesis. Nigam and Batham (Reports of the Indian Science Congress, Agric. Section, 1930) have stated that the nitrification in soils is maximum in the summer and least in the winter. This is easily explained on our hypothesis.

### 56. Studies in photosynthetic activities of various catalysts.

N. A. YAJNIK and F. C. TREHANA, Lahore.

(1) An attempt has been made to corroborate the work of Baly and others and to work out the conditions for the maximum yield.

(2) Experiments have been performed to investigate the possibility of using coloured substances other than those which have already been employed by Baly and his co-workers, and an attempt has been made to compare the catalytic activities of these substances.

(3) The catalytic power of white substances under the influence of visible light has been studied and the influence produced on their catalytic activity by artificially colouring them has also been investigated.

(4) An attempt has been made to study the catalytic activity of white substances under the influence of lights of different colours.

### 57. Inversion of cane-sugar under the influence of tropical sun-light.

N. A. YAJNIK and M. L. WADHERA, Lahore.

(1) Dhar's work on the subject, which has been criticised by Langmuir and others, was repeated and the results corroborate Dhar's experimental observations.

(2) Other catalysts besides hydrochloric acid have also been tried and have been found to accelerate the rate of inversion of cane-sugar.

(3) The results show that light or the catalyst alone is able to bring about the inversion of cane-sugar, but a combination of the two influences accelerates the velocity of inversion.

(4) Preliminary experiments, carried out to examine the effective region of light, show that the region of maximum influence for a catalyst depends probably on the nature of the catalyst.

### 58. Photo-chemical oxidation in unpolarised and circularly polarised light.

J. C. GHOSH, R. PURKAYASTHA, and T. BANERJEE, Dacca.

The photo-chemical oxidation of dextrose by hydrogen peroxide in acid medium with tungstic acid sol as photosensitizer has been studied in (a) unpolarised light, (b) d-circularly polarised light, and (c) l-circularly polarised light of wave-length  $366\mu$ . Monomolecular velocity constants were obtained with respect to hydrogen peroxide and some typical results are recorded in Table I.

Table I.  $T=30^{\circ}\text{C}$

Conc. of dextrose and sol tungstate  $\cdot 025\text{ M}$  each,

Conc. of  $\text{HCl}=\cdot 08\text{ M}$ ; conc. of  $\text{H}_2\text{O}_2=\cdot 02\text{ M}$

	Intensity	Velocity constant
(a) Unpolarised light ..	536 ergs	0.00102
(b) d-circularly polarised light ..	586 ergs	0.00107
(c) l-circularly polarised light ..	586 ergs	0.0015

The great efficiency of l-circularly polarised light is apparent.



59. Action of light on  $\alpha$ -naphthyl-amino-camphor in chloroform solution.

B. N. MITRA.

The paper describes certain experiments carried out with a view to quantitatively investigate the phenomenon of phototropy observed by B. K. Singh in solution (*J. Amer. Chem. Soc.*, 1921, 43, 333; *J.I.C.S.*, 1924-25, 1, 45). As the result of a thorough experimental enquiry it has been found that the case in question does not come under the category of "phototropy" at all. It is a distinct photochemical reaction taking place between the molecules of the solvent and the solute.

60. Chemiluminescence of amarine.

S. S. BHATNAGAR and KRISHNA GOPAL, Lahore.

The spectra of extremely faint luminescence emitted during the reactions of amarine with the halogens have been described. The heats of the reactions are measured and the kinetics of the reactions discussed in the light of the above observations.

61. Chemical reactions under electrodeless discharge.

S. S. BHATNAGAR and R. K. SHARMA, Lahore.

Lead tetra phenyl was exposed to the action of the discharge and the temporary existence of the phenyl radical has been detected.

62. The decomposition of benzene by electric discharge.

S. S. JOSHI and K. K. SHARMA, Benares.

The decomposition was produced by subjecting benzene vapour to ionisation by collision in the annular space between two coaxial tubes sealed together as in a Siemen's ozoniser, due to alternating electric fields of about 50 cycles per second. The progress of the reaction was marked by the deposition of a brown solid on the walls of the discharge tubes. It was necessary to subject the vapour to the discharge for several days before small quantities of the products of decomposition could be obtained. The solid has a characteristic smell, remains apparently unaltered when exposed to air, has a high but not definite melting point, and is distinctly of the aromatic type. It is insoluble in water but very sparingly soluble in the common organic liquids. In addition to the production of this solid body, other products in relatively much smaller amounts accumulate in the reaction vessel. Amongst these one has been identified to be ethyl phenyl acetylene. It was also observed that the nature of the glow in the vapour changed markedly during the progress of the change, presumably as a result of the occurrence of consecutive reactions, subsequent to the principal change.

63. The condition for chemical reactivity in electrical discharge due to alternating fields.

S. S. JOSHI, Benares.

Assuming that in a gas subjected to the discharge, a reactant molecule is changed chemically by collision with an electron possessing a certain minimum critical energy, a theory is given in which the time,  $t$ , during which in a period of alternation the instantaneous values of the applied field exceed a certain minimum, has been found to be the chief determinant of the reaction rate. Other conditions remain-



ing unaltered, it has been deduced that the rate of change is diminished by (i) reducing the applied field, (ii) increasing the gas pressure, and (iii) admixture with gases of marked electron affinity, since each of these factors has been shown to diminish the time,  $t$ . Data are presented in support of this deduction.

#### 64. Influence of position isomerism on diamagnetic susceptibilities.

S. S. BHATNAGAR and R. N. MATHUR, Lahore.

Magnetic susceptibilities of a large number of position isomerides have been determined by an apparatus similar to Bauer and Piccard's U-tube apparatus and the authors' previous observations (*Phil. Mag.*, July, 1930) have been confirmed and extended. In the case of ortho and para or primary and secondary isomerides, it has been shown that the differences between their values for the magnetic susceptibilities increase with the size of the substituent groups. Some isomerides have also been investigated at higher temperatures in order to see if the differences between their values of the magnetic susceptibility are due to the different degrees of their molecular association. And it has been shown that a small difference between the degrees of their molecular association cannot be responsible for the comparatively large differences between the values of their magnetic susceptibilities. If at all, it might be responsible for a very small fraction of these differences. A new explanation, taking into account the radii of the shared orbits between carbon and other atoms in the molecule, has therefore been put forward to explain the different magnetic behaviour of position isomerides.

#### 65. Magnetic susceptibilities of geometrical isomers.

S. S. BHATNAGAR, R. N. MATHUR, and M. B. NEVGI, Lahore.

By a slightly modified and improved form of the magnetic balance described before (Bhatnagar and Mathur, *Phil. Mag.*, December, 1929), geometrical isomers have been investigated and it has been found that their values for the magnetic susceptibility slightly differ from each other. An influence of polymerisation on magnetic susceptibilities has also been observed and an attempt has been made to explain the above facts on the basis of the electronic significance of valency bonds.

#### 66. Influence of temperature on diamagnetic susceptibilities.

S. S. BHATNAGAR and R. N. MATHUR, Lahore.

During the work on position isomerides, it was noticed that the diamagnetic susceptibilities of some liquid isomers vary slightly, but regularly, with temperature. A detailed investigation of organic liquids was therefore undertaken by a very sensitive magnetic balance, and it was found that these changes are observable only in the case of aromatic substances, being of the order of 1.5% for 100°C. difference in temperature. In the case of aliphatic substances the changes are much less and can hardly be accurately observed. It is of interest to note in this connection that the magnetic anisotropy and birefringence also of the aromatics are known to be higher than those of the aliphatics.



## 67. Parachors of some organo derivatives of copper.

S. S. BHATNAGAR, BALWANT SINGH, *and* N. D. SODHI, Lahore.

The new method of obtaining parachors from solutions as employed by Hammick and Andrew has been used for the parachor determination of a large number of copper derivatives of  $\beta$ -diketones and fatty acids and the parachor value for copper has been found to be 45.2. From the value so obtained it has been found that the copper derivatives of  $\beta$ -diketones contain singlet linkages while those of the fatty acids possess an open-chain structure.

The hydrated derivatives of the fatty acids form alcoholates.

## 68. The electronic constitution of some simple and complex derivatives of copper in relation to their magnetic properties.

S. S. BHATNAGAR, BALWANT SINGH, *and* A. G. ASGHAR, Lahore.

Magnetic susceptibilities of copper derivatives of fatty acids,  $\beta$ -diketones, dimethyl glyoxime and ethylene diamine have been determined in solution by Quincke's method and in solid state by Guoy's method. These are found to be paramagnetic while tetra-kis-ethylene thio-carbamido cuprous nitrate is diamagnetic and its susceptibility determined by Curie's method.

Paramagnetism in case of the copper derivatives of fatty acids is due to spin moments of the electrons present in incomplete shell of the central metallic atom. In case of complex derivative of  $\beta$ -diketones, dimethyl glyoxime and ethylene diamine the paramagnetic properties are explained according to Welo and Baudisch's rule.

Diamagnetism in the case of tetra-kis-ethylenethio-carbamido-cuprous nitrate is due to its possessing the inert gas configuration.

## 69. The effect of dilution and the arsenious oxide on the migration velocities of arsenious sulphide sol.

S. S. BHATNAGAR *and* D. C. BAHL, Lahore.

It has been observed that the effect of dilution depends upon the concentration of the sol. In less concentrated sols the speed diminishes on dilution while in concentrated sols the speed increases.

On the other hand the increasing concentrations of arsenious oxide sensitise the sol which is in keeping with observed decrease in the migration velocity of the arsenious sulphide sol.

## 70. Studies in disperse systems.—Part 1: The stability of dilute emulsions.

S. S. BHATNAGAR *and* D. N. GOYLE, Lahore.

In the present investigation attempts have been made to study the influence of the dispersion medium on the stability of dilute Oil-in-Water emulsions in the light of Krulyt's hypothesis. The results of our investigations go to prove that the stability of such systems is governed by the electrokinetic factor only and that the dispersion medium does not exert any stabilising influence on the dispersed oil globules. This conclusion brings the dilute emulsions under the category of lyophobes and strengthens the analogy shown to exist between emulsoids and suspensoids by various other workers to a still closer degree.



## 71. Vanadium catalysts for the contact process.

K. W. KHUBCHANDANI.

Continuing previous work, comparative study of different preparations of vanadium has shown that a catalyst prepared according to the details given by Holmes and Elder (*Ind. Eng. Chem.*, 1930, 22, 471) containing 1.5 per cent. of vanadium, gave at 500° with air containing 7 per cent. of sulphur dioxide and 12 c.c. of catalyst, conversions of 96, 93, 92, and 90 per cent. at gas velocities proportional to the figures 1, 2, 4, and 8.

Corresponding figures for magnesium sulphate impregnated with 0.35 per cent. of platinum were 98.5, 97, 94, and 86 at 430°. The silver vanadate catalyst recommended by Neumann gave no conversion at all.

## 72. On the mechanism of contact catalysis.

K. M. CHAKRAVARTY, Dacca.

It is suggested that a reaction is catalysed by one of the following ways:—

- (a) By individual leptons or leptyles of the catalyst.
- (b) By two or more of such similar or dissimilar leptons and leptyles, the linear distance between them being a determining factor.
- (c) By three or more of such similar or dissimilar leptons and leptyles, the distance and orientation entering into the phenomenon.

In the case of endothermic reaction the major part of reaction is catalysed by the most active particles and the other particles only serve to supply the energy of activation probably through resonance. Whilst in the case of exothermic reaction the active particles not only catalyse the major part of the reaction but also activate the less active ones probably also through resonance. Certain experimental evidences supplied.

## 73. On contact catalyst, promoter and heat of activation.

K. M. CHAKRAVARTY, Dacca.

The fact that in the case of exothermic reactions the promoter helps in stopping the coalescence of the most active particles is further emphasized. It is pointed out that the concentration of the promoter just on the surface of the catalyst needs not always be the same as its average concentration in the catalyst. In the exothermic reaction the most active points may lose activity in case of unpromoted catalysts within the first few seconds after the reaction is started. Attention to these important factors is drawn.

It is suggested that promoter action is due to one or more of the following factors:—

- (a) Increase of the number of active points per unit surface.
- (b) Stoppage of the coalescence of the active particles.
- (c) Actual contribution to the catalytic mechanism.

The total mean energy of a vibrating atom is given by the expression  $4\pi^2mr^2v^2$ . With the help of the factors entering into this expression it has been shown that there exists a simple relation between a catalyst and its promoter where the factor (c) enters. The probability of a connection between the heat of activation and the above expression is also suggested. Certain experimental evidences supplied.



74. On catalysis, specificity in catalysis and efficiency in catalysis.

K. M. CHAKRAVARTY, Dacca.

It is suggested that the above factors are determined by all or by part of the following :—

- (a) Chemical nature of the leptons and the leptyles of the catalyst.
- (b) Leptonic and leptylic diameters.
- (c) Orientation of the leptons and leptyles.
- (d) Number per unit area and the degree of unsaturation of the active particles.
- (e) Orientation of the molecules adsorbed.
- (f) The factors which enter into the energy of vibration of the leptons and leptyles.

Experimental evidences supplied.

75. Catalytic oxidation of paraffins.

M. N. GOSWAMI and S. K. CHATTERJEE, Calcutta.

Vapour of paraffin wax (M.P. 49°C) was passed with air over reduced nickel at 200°C. The product was liquid and the paraffin was eliminated by alcohol, when a liquid was obtained. This gave all the tests of aldehydes, the bisulphite compound on decomposition gave a product which on fractional distillation showed it to be a mixture of higher aldehydes.

Further experiments in this line are in progress.

76. The effect of temperature on the distribution coefficient of some organic acids.

A. B. MALKANI, Benares.

The distribution coefficients of acetic, propionic, benzoic, and phenyl acetic acids have been determined at 17°C, 26°C, 41°C, 50°C, and 60°C. Using the simple Nerust's equation for calculating the distribution coefficient, it has been found that to a first approximation the coefficient is an exponential function of the temperature.

77. Reaction in mixed solvents and neutral salt effect. Inversion of cane sugar.

A. GANGULI and A. B. MALKANI, Benares.

The velocity of inversion of cane sugar by decinormal HCl in mixed solvents as well as in presence of small quantities of electrolytes was determined polarimetrically. The pH of the corresponding solutions were also found electrometrically. As expected from Hückel's theory the activity of the H ion concentration increases regularly with the conc. of the electrolyte as well as non-electrolyte present, on account of the diminution of dielectric constant. In the case of electrolytes, the velocity of sucrose inversion increases with the conc. of electrolyte (neutral salt effect) whereas in the case of non-electrolytes, such as alcohols, certain peculiarities are observed. The velocity coefficient rises in the beginning with increasing conc. of alcohol, attains a maximum and finally diminishes with further increase of concentration. This might be due to hydrate formation with the alcohols, thus the molecules of water that take part in the reaction are removed. Viscosity may also play an important rôle with highly conc. sucrose solution hydration factor again comes in and the reaction is not strictly mono-molecular. Thus it is postulated that



there are three factors which control the rate of inversion of sugar: (a) hydration, (b) lowering of dielectric constant, and (c) viscosity.

78. Esterification equilibria in the vapour phase.

S. K. KULKARNI JATKAR and N. G. GAJENDRAGAD,  
Bangalore.

In continuation of previous work, the esterification equilibria between the vapours of methyl, ethyl and propyl alcohols and acetic acid have been investigated at  $230^{\circ}$  and  $260^{\circ}$  in presence of silica and potassium alum as catalysts. Equilibrium was approached from both directions and the composition of the reacting mixture varied within wide limits. The following values for the equilibrium constant were obtained: methyl alcohol and acetic acid at  $230^{\circ}$  with alum 9, and with silica 25. Ethyl alcohol and acetic acid at  $230^{\circ}$  with alum 9, and with silica 8; at  $260^{\circ}$  with silica 9. This reaction is complicated by the formation of ethyl ether when alum is used as the catalyst. In the case of propyl alcohol, both propylene and propyl ether were produced and the esterification constant could not be determined.

79. Kinetics of the decomposition of trichloroacetic acid in aqueous solutions.

A. N. KAPPANNA, Nagpur.

Previous investigators have shown that trichloroacetic acid decomposition follows the unimolecular law. The present investigation was undertaken with a view to find out if the reaction was an ionic one. In very dilute solutions the unimolecular velocity constant  $k$  is almost independent of concentration, but as the concentration of the acid increases the value of  $k$  gradually falls. Effect of neutral salts and cane sugar on the velocity of decomposition has been determined. The temperature coefficient of the velocity constant is independent of the concentration of the acid in presence of neutral salts or cane sugar. A mechanism for the reaction has been suggested which quantitatively accounts for the observed variation of  $k$  with concentration of the acid.

80. Decomposition potentials of 'dilute hydrochloric acid solutions at different temperatures and concentrations.

A. N. KAPPANNA, Nagpur.

The investigation is an extension of the work of Le Blanc on the subject. An attempt has been made to determine accurately the limiting values for the decomposition potential of hydrochloric acid in aqueous solutions at different temperatures. The experimentally determined values for the decomposition potentials at different concentrations agree well with values calculated from theoretical considerations.

81. Role of phosphates in the oxidation of glucose.—Part II.

A. N. KAPPANNA and R. N. KAYASTH, Nagpur.

The investigation is an extension of the work published by one of the authors (*J.I.C.S.*, 1928). A study of the kinetics of the oxidation of glucose by hydrogen peroxide in phosphate buffer mixtures has been made. The results agree to a great extent with the results obtained previously by Witzemann (*Journ. Biol. Chem.* 1. 45. 1920).



## 82. Potential and energy of chemical reaction.

J. N. RAKSHIT, Gajipur.

A discussion about the unsuitability of measurement of chemical energy and chemical potential of chemical reaction by means of the determination of electromotive force by various methods.

All phenomena connected with the experiments for the determination of hydrogen ion concentration have been proposed to be explained by the application of the author's association theory of solution.

## 83. A new sensitive indicating device for use in electrolytic conductivity bridge.

N. NARASIMHAMURTY and M. SREENIVASAYA, Bangalore.

An oxide rectifier type of A.C. micro-ammeter is used as the indicating instrument instead of the ear-phones. The small voltage is amplified by the use of a Loewe 3 N.F. valve, and the output is fed to the indicating instrument through a choke capacity filter arrangement. All stages are efficiently decoupled to prevent low-frequency reaction, and the grid bias for all the stages are derived automatically from the filament and anode currents.

The apparatus embodies a D.C. eliminator unit for obtaining high tension from the mains.

## 84. Two new valve potentiometers for use in electrometric titrations and in the measurement of hydrogen-ion-concentration.

N. NARASIMHAMURTY and M. SREENIVASAYA, Bangalore.

The essential feature of the first type of instrument is a pair of pentode valves arranged in a push-pull manner. The anode battery, filament battery and the steady bias battery are common to both valves. On the grid of one of the valves is superimposed the unknown voltage and a model 45 Weston milliammeter connected between the anodes of the two valves is the indicating instrument. The instrument is calibrated in terms of both volts and pH.

The second type of instrument consists of the same arrangement but makes use of another valve of high internal resistance, coupled through a resistance to one of the valves in push-pull. The arrangement is sensitive to small voltages and can be used in measurements involving glass electrodes, etc.

## 85. Decomposition of phenol and naphthol ethers when heated with concentrated hydrochloric acid.

G. B. KOLHATKER and R. P. GHASWALLA, Poona.

Phenolic ethers with different substituents in the meta, ortho and para positions in the benzene ring and ethers of naphthols were treated in sealed tubes with 10N. hydrochloric acid at 130°C for two hours and the extent to which they decompose was determined.

Ethers with different substituents in the meta position decomposed to the least extent, those with the substituents in the para position decomposed to the greatest extent and those with the substituents in the ortho position showed an intermediate decomposition.

Studying the influence of the nature of the substituents on the decomposition it was found that bromo, chloro, and nitro groups increase considerably the stability of the ethers. Methyl group also in-



creased the stability a little. Amino and acetyl groups decreased the stability of the ethers in the ortho and para positions.

The influence of the substituting groups on the stability of the ether was the greater, the greater the number of such groups in the benzene ring.

Ethers of  $\beta$ -naphthol decomposed more readily than those of  $\alpha$ -naphthol and as may be expected methyl ether of aromatic tetra-hydro  $\alpha$ -naphthol decomposed much less than the corresponding methyl ether of  $\alpha$ -naphthol.

### 86. The interaction between iodine pentoxide and nitric oxide.

M. S. SHAH and T. M. OZA, Ahmedabad.

The interaction between iodine pentoxide and nitric oxide has been studied at 120°. Iodine is evolved and in presence of sodium-hydroxide all the gas is converted into nitrite and nitrate.

From (i) the amount of iodine produced and (ii) the amount of nitrite formed, the volumes of nitric oxide are calculated and found to be in agreement with the volumes of nitric oxide used in the experiments.

The mechanism of reaction is discussed.

### 87. Nitrito-phosphites and Nitrito-hypophosphites.

P. NEOGI and M. N. PHUKHAN, Calcutta.

Nitrito-phosphites and nitrito-hypophosphites of some metals have been prepared.

### 88. Halogenation.—Part VIII: Bromination of benzene in sun-light.

P. S. VARMA and H. C. SINHA, Benares.

Benzene is not brominated directly in the dark nor in diffused day-light to any appreciable extent. In direct sun-light, however, in addition to benzene hexabromide, considerable quantities of mono-, bromo- and di-bromo-benzenes have been obtained. Starting with 200 c.c. of benzene and 40 c.c. of bromine, on 65 hours' exposure to direct sun-light, about 31 c.c. of bromo-benzene, 15 c.c. of dibromo-benzene and 65 grams of benzene hexabromide have been obtained.

### 89. Halogenation.—Part IX: Bromination of benzene in presence of halogen carriers and sun-light.

P. S. VARMA and H. C. SINHA, Benares.

More than hundred experiments have been carried on in which benzene and bromine have been kept for different lengths of time in contact with a number of substances such as iron, aluminium, antimony, zinc, tin, magnesium, aluminium mercury couple, sulphur, ferric oxide, iodine, pyridine, zinc chloride, aluminium chloride, ferric chloride, nitric acid, strong or fuming sulphuric acid, etc., in the dark or in diffused day-light or in direct sun-light. Very little action has been found to take place in the dark. Some action takes place in diffused day-light but the action in sun-light is much more prominent. The main product obtained in the case of sun-light is mono-bromo-benzene. In some cases di- and tri-bromo-benzenes have also been obtained. It is curious that no addition compound with benzene is obtained to any appreciable extent. A halogen carrier, combined with sun-light, seems to be capable of producing a better yield of the bromo-derivatives.



90. Halogenation—Part X. Bromination and iodination of the fatty acids.

P. S. VARMA and S. MENON, Benares.

It has been possible to get up till now comparatively a good yield of the bromo- and iodo- derivatives of the lower fatty acids when the fatty acids or their anhydrides are treated with bromine or iodine in presence of strong sulphuric acid. Experiments have been carried on in presence of other substances also but the best yield so far obtained is in presence of strong sulphuric acid only.

91. Halogenation—Part XI. Halogenation of azo- and hydrazo-benzene.

P. S. VARMA and V. K. B. BENON, Benares.

A number of experiments have been carried on the direct iodination of azo-benzene but no definite result has yet been obtained. With hydrazo-benzene, however, some definite compounds about which we do not find any mention in the chemical literature, have been obtained with chlorine and bromine under certain conditions. The investigation of these compounds is in progress.

92. Molecular rearrangement during bromination. Preparation of 3:5-dinitro-2-hydroxy-4-methoxybenzaldehyde and its bromination.

M. SESHAIYENGAR and K. SANTANAM, Bangalore.

The above dinitro-aldehyde was best prepared by heating a solution of 5-nitro-2-hydroxy-4-methoxybenzaldehyde in glacial acetic acid with fuming nitric acid and the crude product that was obtained was purified by preparing its sparingly soluble potassium salt, acidifying it and recrystallising from dilute acetic acid. Long colourless needles were obtained melting at 128°–129°. The oxime forms light yellow needles melting at 182°. Bromination of this dinitro-aldehyde yielded a dibromo-product (m.p. 127–128°) identical with 2:6-dibromo-4-nitro-resorcinol monomethyl ether obtained by brominating 6-nitroresorcinol-3-monomethyl ether, thus serving as another instance to show that a molecular rearrangement should have taken place during bromination.

93. Studies on Reimer and Tiemann's reaction.

R. N. SEN and S. Roy, Calcutta.

It has been found that chloroform or carbon tetrachloride, when mixed with sufficient quantity of alcohol (1:3), greatly increases the yield of the hydroxy aldehydes of acids in Reimer and Tiemann's reaction (from 18% to 31% in the case of Salicylaldehyde and from 5% to 12% in the case of Salicylic acid); and in some cases (*e.g.* nitrophenols, *o*-bromophenol, naphthol) the use of pyridine also facilitates the reaction.

It has also been observed now that, Reimer and Tiemann's reaction proceeds smoothly in the presence of aqueous pyridine without using any caustic alkali; thus salicylaldehyde can be prepared with an yield of 10%, replacing caustic soda entirely by pyridine, *p*-hydroxy benzaldehyde being not formed at all.

The influence of the substituents such as NO<sub>2</sub>, Cl, Br, SO<sub>3</sub>H in different positions in the phenols on the reaction has been thoroughly studied, the substituents generally exerting more or less inhibiting action, the nitro group having the greatest effect.



Further the reaction has been successfully applied to ortho-coumaric acid, thiophenol, oxyquinoline and oxy-anthra-quinone; ortho-coumaric acid giving with chloroform 5-aldehydo-ortho-coumaric acid decomposing at  $220^{\circ}\text{C}$ . and thiophenol giving thiosalicylic acid (3.5%) with carbon tetrachloride; 8-oxy-quinoline yielding readily with chloroform 16% ortho and 30% para-aldehyde, and 2-oxy-anthraquinone producing 25% ortho aldehyde.

#### 94. Extension of Michael's reaction—Part III.

T. N. GHOSH and P. C. GUHA, Bangalore.

In order to study the reactivity of systems containing azo-groupings, phenylazo carboxylic ester ( $\text{PhN} : \text{N} - \text{COOEt}$ ) and ethylazo-dicarboxylate have been condensed in presence of sodium and dry ether with urethane, acetoacetic ester, acetylacetone, cyanacetic ester, etc., and compounds of the type  $\text{RNX} - \text{NH} \cdot \text{COOEt}$  ( $\text{R} = \text{Ph}$  or  $\text{COOEt}$ ;  $\text{X} = -\text{NH} \cdot \text{COOEt}$ ,  $\text{CH}_2 - \text{CO} - \text{C}_6\text{H}_5 - \text{COOEt}$ ,  $-\text{CH}(\text{COCH}_3)_2$ ,  $-\text{CHCN} \cdot \text{COOEt}$ ) have been obtained. Azobenzene does not react. The conclusion to be drawn from these results is that one or both of the groups attached to the azo complex  $-\text{N}=\text{N}-$  must be strongly electronegative. Further work in this line with unsaturated systems like  $\text{RCH}=\text{NR}$  is in progress.

#### 95. The use of acid anhydrides in the Nencki method for the preparation of phenolic ketones.

A. S. BHULLAR and K. VENKATARAMAN, Lahore.

The Nencki method of heating phenols with acids and zinc chloride gives unsatisfactory yields of ketones in many cases. The use of a mixture of acid and acid anhydride leads to greatly improved results. Resacetophenone and gallacetophenone may thus be prepared in 60–70% yield. Employing this modification, the preparation of several new ketones (phenyl acetophenone,  $\omega$ -methoxygalacetophenone,  $\omega$ -methoxyacetophenone, etc.) is described. Our interest in these ketones is in their conversion to various polyhydroxy flavones.

An attempt, so far unsuccessful, has been made to apply this reaction to the synthesis of chalcones. The interaction of resorcinol with cinnamic acid, cinnamic anhydride, and zinc chloride has led only to dicinnamoyl resorcin and complex colouring matters. Dutta and Watson (*J.C.S.*, 1911) claim to have prepared chalcones by heating resorcinol (and pyrogallol) with cinnamic acid and zinc chloride. Ellison (*J.C.S.*, 1927) and we have been unable to repeat the result.

#### 96. On the activity of chloropicrin on arylamines.

M. N. RAMASWAMI and P. C. GUHA, Bangalore.

Describes the action of arylamines on chloropicrin, attention being directed to the effect of the substitution of  $\text{RNH}$ -groups in place of chlorine atoms in the molecule.

#### 97. Formation of thiophene derivatives from acetonyl sulphide.

D. N. MAJUMDAR and P. C. GUHA, Bangalore.

When pinacone condensation under varying conditions was being tried with acetonyl sulphide and phenacylsulphide in this laboratory, a paper was published by Matthaiopoulos and Sagniaris (*J. Pr.* 1929, 123, 333). Phenacylsulphide remained unconverted due evidently to the proximity of two phenyl groups to the ketonic groups; but from



acetonysulphide two products, one soluble and the other insoluble in alkali, have been obtained. Work on the preparation of phenacyl, methacyl, imine, and oxide is in progress.

98. The Condensation of m-Hydroxy benzoic acid and its methyl ether with Chloral.

M. S. SHAH, Ahmedabad.

When chloral is condensed with m-hydroxy benzoic acid and its methyl ether in presence of sulphuric acid 5-hydroxy-trichloromethylphthalide, m.p.  $200^{\circ}$  (I), and 5-methoxy-trichloromethylphthalide, m.p.  $135^{\circ}$  (II), are produced. In the former case if sulphuric acid is present in excess sulphonation proceeds along with chloral condensation and the product appears to be 4-sulpho-5-hydroxy-trichloromethylphthalide, m.p.  $246^{\circ}$  (III).

The action of hot aqueous alkalis gave tarry product from I, 5-methoxyphthalide-carboxylic acid, m.p.  $170^{\circ}$ , from II and 4-sulpho-3-hydroxy benzoic acid from III, indicating that chloral was loosely held in III. Elimination of carbon dioxide from 5-methoxyphthalide-carboxylic acid and subsequent oxidation with alkaline potassium permanganate gave rise to 5-methoxyphthalide, m.p.  $120^{\circ}$ , and 5-methoxyphthalic acid, m.p.  $164^{\circ}$ , respectively. The substance II and its products are identical to those described by Fritsch (Ann., 1897, 296, 344).

The condensation products I and II were reduced with zinc and acetic acid so that  $-\text{CH}(\text{OH})\text{CCl}_3$  became  $-\text{CH}_2\text{CHCl}_2$ . Subsequent treatment of the products with sulphuric acid led to hydrolysis and oxidation as observed by Meldrum and Vaidyanathan (Proc. Ind. Sc. Con., 1929, p. 133) and  $-\text{CH}_2\text{CHCl}_2$  became  $-\text{CH}_2\text{COOH}$ . The hydroxy products of I gave, on treatment with dimethylsulphate, the methoxy products of II. The final products, 5-hydroxy and 5-methoxy homophthalic acids, when oxidised with alkaline permanganate resulted in the breakdown of the molecules into carbondioxide. Attempts to get hydroxy and methoxy phthalic acids by oxidation are in progress.

99. Studies in thiol series. Part I. Derivatives of (a) o, m, and p-methoxytoluenes and (b) o, m, and p-methoxy benzoic acids.

M. S. SHAH, C. T. BHATT, and D. D. KANGA, Ahmedabad.

(a) The isomeric thiol derivatives of o, m, and p-methoxytoluenes have been prepared from the corresponding sulphonic or sulphinic acids by the usual method. The sulphonic acids were obtained by sulphonation of methoxytoluenes and sulphinic acids were derived from the amino-methoxytoluenes by Gattermann's method (Ber., 1899, 32, 1136). On methylation the thiols gave the methylthiols which, when oxidised with potassium permanganate in alkaline solution, produced characteristic methoxy-benzoic-acid-methylsulphones possessing sharp melting points.

(b) Isomeric sulpho- o, m, and p-hydroxy benzoic acids were methylated and their methyl ethers converted into the corresponding thiols. These passed on methylation and subsequent oxidation into methylthiol-methoxy-benzoic acids and methoxy-benzoic-acid-methylsulphones respectively. The latter were identical with the methylsulphones described in (a): the admixture of the two in no case showed any depression in melting point.

The identity of methylsulphones in (a) and (b) gives a method, alternative to that of sulphonamide, for checking the constitutions of sulphonic acids.



## 100. Reaction of urethane with acid chloride.

P. S. MAYURANATHAN and P. C. GUHA, Bangalore.

The ordinary method of preparing acetyl urethane is by heating a mixture of urethane and acetyl chloride in a sealed tube at 100–120°C for 4 hours. But it has now been found that a quantitative yield of the product can be obtained by simply mixing the ingredients and keeping overnight. Similarly, for the preparation of benzoyl urethane a method has been evolved by which an yield of 40 per cent. is obtained (yield according to older method being 15%). An attempt to bring about the inner condensation of benzoyl-urethane has resulted in the formation of benzamide. Benzene sulphonylchloride reacting with urethane, however, yields benzene sulphonylallophanic ester ( $\text{PhSO}_2\text{-NH-CO-NH-COOEt}$ ). Condensation of benzoylchloride with amino-sulphonic ester and the ring closure of the resulting product with a view to get saccharine is being studied.

## 101. Derivatives of carbazinic ester and their ring closure.

D. N. MAJUMDAR and P. C. GUHA, Bangalore.

Carbazinic ethylester ( $\text{NH}_2\text{-NH.COOEt}$ ) has been condensed with aldehydes, ketones, acid chlorides, halogen substituted acid esters, Ketonic esters, isocyanates, thiocarbamides, and several of these condensation products have been made to yield heterocyclic compounds by the action of suitable ring closing agents.

## 102. Condensations of chloral and trichloro-acetic acid with phenols.

R. N. SEN and S. ROY, Calcutta.

Chloral reacts with phenol in aqueous pyridine solution at the temperature of the boiling water bath yielding: O-hydroxy-benzoyl formaldehyde  $\text{OH.C}_6\text{H}_4\text{.CO.CHO}$ , orange liquid boiling at 175° (Di-semicarbazone, m.p. 246°).

By heating an alkaline solution of the phenols with trichloroacetic acid on the water bath at 70–80° Keto-acids are formed. Thus phenol gives 6% ortho-hydroxy phenyl glyoxylic acid decomposing at 95° (Semicarbazone decomposes at 237°) and splitting off  $\text{CO}_2$  by heating at 150° for half an hour to produce salicylaldehyde; and 2% para-hydroxy phenyl glyoxylic acid m.p. 170°C, found to be identical with the compound prepared from para methyl-phenyl-hydroxy-glyoxylic acid (Boaveault, Bull. Soc. Chim. 1898, (iii) 19, 75); the ortho compound on keeping for some days passes into the lactone.  $\beta$ -naphthol yields 10% 2-hydroxy- $\alpha$ -naphthyl-glyoxylic lactone, yellow needles m.p. 184° (Semicarbazone: m.p. 240°), identical with the compound prepared from phenyl carbylamine and  $\beta$ -naphthol (Passerini, Gazzetta, 1924, 54, 184). It gives a deep red coloration with concentrated sulphuric acid which becomes greenish with a trace of thiophene (cf. Isatin).

## 103. Condensation of cyanacetic ester with mesityl oxide.

P. S. MAYURANATHAN and P. C. GUHA, Bangalore.

Condensation of mesityl oxide and cyanacetic ester and its methyl substitution product (cf. Vorlander, Ann. 1897, 294, 253, and Kohler J.A.C.S., 1923, 45, 1987) was studied with the result that cyanodimethyl-dihydroresorcin and its methyl substituted derivative were obtained; their identity was proved by synthesis from the corresponding additive products as also by their conversion into dihydro-resorcins. The cyano-



dimethyldihydroresorcins exist only in the enolic form, for they fail to give derivatives with semicarbazide and hydroxylamine but they give acetyl derivatives. The additive product ( $\alpha$ -cyano- $\beta$ - $\beta$ -dimethyl- $\gamma$ -aceto-butyrates) gives the  $\alpha$ -bromo-compound with bromine which with potassium acetate is converted into a cyclopropane derivative which has also been obtained from the  $\alpha$ -dibromo-compound.

#### 104. Condensation of benzotrichloride with phenols.

R. N. SEN and S. ROY, Calcutta.

Fritz Heiber (Ber., 24, 3677) obtained in a very poor yield (about 1%) ortho-oxybenzophenone by the reaction between phenol and benzotrichloride under Reimer and Tiemann's condition. It has now been found that an alcoholic solution of benzotrichloride (3:1) reacts with an alkaline solution of phenol at the temperature of the boiling water bath yielding 5% ortho-oxybenzophenone. The nitrophenols do not react with benzotrichloride. With  $\alpha$ -naphthol two products are obtained:

(1) Para-hydroxynaphthylphenyl ketone (4%) soluble in alkali melting at 163-164° (forming a phenylhydrazone and a semicarbazone identical with the compound, prepared from 1-hydroxy-naphthyl-2-carboxylic acid and benzotrichloride (D.R.P. 378908, 3789909); Swiss Pat. 98559); and (2) ortho-hydroxynaphthylphenyl ketone (16%) m.p. 114° insoluble in alkali, which does not react with phenylhydrazine and semicarbazide.  $\beta$ -naphthol also reacts with benzotrichloride producing 2-hydroxy- $\alpha$ -naphthylphenyl ketone (20%) (m.p. 174°), identical with the compound previously prepared from  $\beta$ -naphthol and benzotrichloride without any alkali (D.R.P. 378908, 378909). Ortho-Coumaric acid readily reacts with benzotrichloride forming *o*-coumarylphenyl ketone (30%) decomposing at 183° (phenylhydrazone decomposing at 120°).

#### 105. Condensation of cyclohexanone with resorcinol and other aromatic hydroxy-compounds.

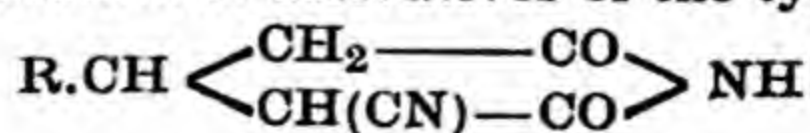
R. N. SEN and J. SARDAR, Calcutta.

By condensing one molecule of cyclohexanone with two molecules of aromatic hydroxy compounds such as *p*-cresol, *m*-cresol, resorcinol, pyrogallol, dimethyl-*m*-aminophenol, and para-cresotinic acid in the presence of zinc chloride and hydrochloric acid gas at 140-180°C compounds with pyrone ring formation have been obtained, in which the central carbon atom forms a member of two different rings analogous to the spiro-compounds and is also attached to four carbon atoms analogous to tetraphenyl methane derivatives. Some of these compounds are beautiful dyes, the resorcinol compound dyeing wool and silk a brownish-orange shade (bromo-derivative, red shade), the pyrogallol compound a brownish-black shade on iron mordanted wool, and the compound with dimethyl-*m*-aminophenol producing reddish-violet shade. The tinctorial character of these compounds is very remarkable in view of the fact that they do not contain any so-called chromophore nor do they admit of any quinonoid configuration according to the usual modes of tautomerisation.

#### 106. Reactivity of conjugated systems.—Part III.

CHITTARANJAN BARAT, Calcutta.

In continuation of previous works in this series (J. Indian Chem. Soc., 1930, 7, 321; etc.) cyanoacetamide has been condensed with esters of unsaturated acids of the type  $R.CH=CH.COOR$ , ( $R=CH_3, C_6H_5, C_6H_4.NO_2(p)$ , etc.) when glutarimide derivatives of the type—





have been obtained. On hydrolysis, the ring opens out leading to the formation of  $\beta$ -substituted glutaric acids. Attempts are in progress to hydrolyse the cyano-group without rupture of the piperidine ring, and to obtain 2:6-dihydroxypyridine derivatives by dehydrogenation of the original condensation products.

#### 107. Reactivity of conjugated system.—Part IV.

CHITTARANJAN BARAT, Calcutta.

With a view to decide whether hydroxymethylene ketones of the type  $R.CO.CH=CHOH$ , (enolic form) react with a reactive methylene group as in cyanoacetamide, in their enolic or aldehydic forms ( $R.CO.CH_2.CHO$ ), such ketones have been condensed with cyanoacetamide resulting in the formation of 3-cyano-6-R-2-pyridones, which upon hydrolysis gives rise to 2-hydroxy-6-R-pyridines. The evidence so far obtained, though not yet conclusive, indicates that the ketones react in their enolic forms. Further work to substantiate this statement on firmer grounds is in progress.

#### 108. Lengthened ortho-di-derivatives of benzene and their ring-closure. Part VI. Formation of heterocyclic compounds from aryl-carbamidobenzoic acids.

T. N. GHOSH, Bangalore.

Aryl-thiocarbamidobenzoic acids have been obtained by the condensation of anthranilic acid with various mustard oils. While studying the influence of different ring-closing agents upon these compounds, it has been found that strong sulphuric acid at 125-130° effects the ring-closure through the sulphur atom to yield a thiazine derivative, whereas acetic anhydride does the same through the nitrogen atom to yield a diazine derivative—a molecule of water being eliminated in each case. Uraminobenzoic acid loses a molecule of water on being heated with strong hydrochloric acid yielding o-benzoylenurea.

#### 109. Lengthened ortho-di-derivatives of benzene and their ring-closure. Part VII. Synthesis of heptathiodiazines and triazoles.

T. N. GHOSH, Bangalore.

In continuation of a previous work (Ghosh and Guha, J. Indian Chem. Soc., 1929, 6, 181-195) the action of  $\omega$ -bromacetophenone, phosgene, nitrous acid upon 1-o-aminophenyl-3-aryl-thiocarbamides has been studied. 1-o-Aminophenyl-3-phenylthiocarbamide reacts with  $\omega$ -bromacetophenone to yield a compound (m.p. 230° decomp.) which, in the light of available experimental evidence, is ascribed to be 2:2-phenyl-bromomethyl-4:5-benzo-7-keto-1:3:6-heptathiodiazine. 1-o-Aminophenyl-3-arylthiocarbamides react with phosgene and nitrous acid to yield heptathiodiazine and triazole derivatives respectively.

#### 110. Metallic cadmium as a synthetic reagent.

A. C. CHATTERJEE and S. DUTT, Lucknow.

Metallic cadmium in a finely divided state has been found to react vigorously with oxygenated and halogenated compounds in accordance with the well-known reactions of Ullmann, Friedel-Crafts, Wurtz, Reformatski, Claisen and others. It has also been found to act as a strong pyrogenic and neutral reducing agent. In all the above reactions cadmium behaves just like zinc with only slightly diminished vigour, but in many cases the yield of the final product is greater than when zinc is used



instead. The only point in which cadmium differs from zinc, however, is that it refuses to form any well-defined organo-metallic derivative.

### 111. Metallic tungsten and molybdenum in organic synthesis.

G. S. BOSE and S. DUTT, Lucknow.

Both molybdenum and tungsten behave like chromium in most of the typical organic reactions that have been studied. In the wet reactions molybdenum seems to be more reactive than tungsten, though both form the same type of halogen compounds. But still they are much less reactive than metals of the lower groups, such as sodium potassium, magnesium, zinc, aluminum, etc. In pyrogenic, that is dry reactions, both the metals have been found to be very reactive. They can be used in some of the catalytic reductions as well. Both can, for example, reduce benzene giving hydrogenated products, though the yield is much lower than what can be obtained by the Sabatier and Senderen's process.

### 112. Possible methods for the synthesis of isoflavones.

I. C. BADHWAR, B. K. MENON, NATHU RAM, and  
K. VENKATARAMAN, Lahore.

Several representatives of the isoflavone group having recently been shown to occur in nature (*e.g.*, genistein, irigenin, pseudo-baptigenin), the synthesis of isoflavones has assumed interest and importance. The two methods available, both due to Baker and Robinson (J.C.S., 1925 and 1929), are admittedly beset with experimental difficulties and give poor yields. We have undertaken an investigation of other possible methods.

Späth and Lederer (Ber., 1930, 63, 743) claim to have prepared 7-hydroxyisoflavone by condensing ethyl formate with phenyl resacetophenone, but no experimental details are given. This reaction, as well as the condensation of the same ketone with ethyl oxalate, was tried by one of us some years ago, but with negative results.

The following new methods are being studied:—

- (1) The action of trichloroacetic anhydride and sodium trichloroacetate on phenylresacetophenone. The hydrolysis of the 2-trichloromethyl-7-hydroxy-isoflavone to the 2-carboxylic acid has presented difficulties which have not been surmounted.
- (2) The reaction between 2:4-dinitrobromobenzene and the sodium salt of oxymethylenephénylacetic ester.
- (3) The reaction between the sodium salt of resorcinmonomethyl ether and bromatropic acid.
- (4) The condensation of salicylic ester with phenylpyruvic ester.

### 113. A synthesis of 7:8:3':4':5'-pentahydroxyflavone and related flavones.

I. C. BADHWAR and K. VENKATARAMAN, Lahore.

In an earlier communication (J.C.S., 1929) we have reported the synthesis of 7:8-dihydroxy-2-methylchromone and of 7:8-dihydroxyflavone. These flavones derived from pyrogallol have interesting dye-properties and the synthesis of 7:8:3':4':5'-pentahydroxyflavone is now described. The Robinson reaction of trimethyl gallic anhydride and gallacetophenone gave a product difficult to purify; we have, therefore, condensed gallacetophenone-3:4-dimethyl ether with trimethyl gallic ester and sodium and heated the resulting  $\beta$ -diketone with hydriodic acid.

For comparison with this flavone, 5:7:3':4':5'-pentahydroxyflavone and 3:7:3':4':5'-pentahydroxyflavone have been synthesised by heating



phloracetophenone and  $\omega$ -methoxyresacetophenone respectively, with a mixture of trimethylgallic anhydride and sodium trimethylgallate, alkaline hydrolysis and demethylation of the products. 5 : 7 : 3' : 4' : 5'-Pentahydroxyflavone has previously been synthesised (Gaz., 1913) by a different method.

The reactions and dyeing properties of these pentahydroxyflavones and their methyl ethers are described.

#### 114. An attempted synthesis of isoflavones.

I. C. BADHWAR, B. K. MENON, and K. VENKATARAMAN, Lahore.

Although Baker and Robinson have shown that the condensation of oxymethylene benzyl cyanide or oxymethylene phenylacetic ester leads only to coumarins, the problem appears to be worth further study. We have used benzoyl oxymethylene benzylcyanide in conjunction with resorcinol, its monomethyl and dimethyl ethers, the diacetate, dibenzoate, and the dibenzyl ether, the experimental conditions being those of a Hoesch reaction for the synthesis of phenolic ketones. With resorcinol monomethyl ether a trace of 7-methoxyisoflavone could be isolated; in all other cases coumarins were obtained, sometimes together with substances of undetermined constitution. Phloroglucinol gave only 5 : 7-dihydroxy-3-phenylcoumarin. While it is well known that pyrogallol will not undergo a Hoesch reaction, it condensed readily with benzoyl oxymethylene benzyl cyanide, yielding 7 : 8-dihydroxy-3-phenylcoumarin. The interaction of the same nitrile with naphthols is being studied.

Employing glacial acetic acid as the solvent, diacetyl resorcin and benzoyl oxymethylene benzyl cyanide as reactants neither coumarin nor chromone, but a good yield of pale-yellow needles (m.p. 182°) was obtained. From its properties we consider it likely to be oxymethylene phenyl resacetophenone. Attempts at closing up the ring to form 7-hydroxyisoflavone have so far been fruitless.

#### 115. On spiro-compounds.

P. K. PAUL, Calcutta.

The spiro-cyclopropane compounds with substituted cyclohexane as partner are peculiarly unstable, and so the following work for the synthesis of spiro-cyclobutane compounds having cyclohexane, cyclopentane and substituted cyclohexanes as partners was taken up. The synthesis was achieved by following the work of Carl A. Kerr (J. Amer. Chem. Soc. 1929, 51, 617)

Guareschi compounds from cyclohexane, 3-methylcyclohexane and 4-methylcyclohexane were each condensed with  $\text{CH}_3\text{I}$  and the condensation products melted at 266°, 259°, 250° respectively, which were then completely hydrolysed with 20% caustic soda when corresponding spiro-tetracarboxylic acids melting at 190° (decom), 170° (decom), 159° (decom), were obtained. The spiro-tetracarboxylic acids melting at 190° and 170° on elimination of carbon dioxide yielded a mixture of cis and trans spiroacids. The trans acids melt at 178° and 175° respectively. The cis acids have yet not been obtained in a solid crystallisable condition.

Further work in the line are in progress.

#### 116. Synthesis in the anthrone series.

P. K. PAUL, Calcutta.

1 : 3-Dimethoxy-4-methyl-5 : 6-phthalide and 1 : 2 : 3-trimethoxy-5 : 6-phthalide were condensed with methoxy-meta-cresotinic acid ethyl ester in presence of aluminium chloride (J. Amer. Chem. Soc. 1927, page 563) and the partially demethylated benzyl benzoic acid derivatives melting at



204° and 135° were obtained. The ring closure to yield the corresponding anthrones has not yet been achieved. 3:5-Dioxy-4-methylbenzoic acid was methylated with dimethyl sulphate m. p. 144°, which on treatment with formaldehyde in presence of hydrochloric acid gave the corresponding phthalide m.p. 104°. Further work on the line is in progress.

#### 117. Dicoumarin or 6-6'-Dicoumaryl.

R. N. SEN and D. CHAKRAVARTI, Calcutta.

The dicoumarins, 3-3'-dicoumaryl and 4-3'-dicoumaryl, where two coumarin nuclei are linked by the lactone rings, were previously obtained, the former by Dyson (J.C.S. 1887, 51, 62) and Fittig (Annalen, 1889, 255, 1) and the latter by Dey and Row (J. Indian Chemical Soc. 1, 107). The true dicoumarin of the type of diphenyl (6-6'-dicoumaryl), in which two coumarin residues are linked by the benzene nuclei, has now been prepared by heating 6-iodo-coumarin with copper powder at 220°. It is a colourless solid softening at 290° and completely at 245°, difficultly soluble in ordinary organic solvents except pyridin. It is insoluble in isodium carbonate and bicarbonate solutions but dissolves in hot caustic alkalis and also in sodium bisulphite solution like coumarin. Further work is in progress.

#### 118. Coumaro- $\gamma$ -pyrones.

R. N. SEN and D. CHAKRAVARTI, Calcutta.

The authors previously synthesised coumaro- $\alpha$ -pyrones (Proc. Ind. Sc. Congress, 1929; J. Indian Chem. Soc. 6, 793) in which two  $\alpha$ -pyrone rings are condensed with the same benzene nucleus. Coumaro- $\gamma$ -pyrones, where one  $\alpha$ -pyrone ring and one  $\gamma$ -pyrone ring are attached to the same benzene nucleus, have now been obtained by the action of malic acid on hydroxychromones and hydroxyflavones and isoflavones.

#### 119. A synthesis of naphthopyrones.

A. S. BHULLAR and K. VENKATARAMAN, Lahore.

While in the benzene series the Allan-Robinson synthesis of flavones takes place only with phenolic ketones containing at least two hydroxyls in the m-position to each other, 2-aceto-1-naphthol condenses readily with acid anhydrides to give naphtho- $\gamma$ -pyrones. We have thus prepared 2-methyl-naphthopyrone, naphthoflavone and 4'-methoxynaphthoflavone. A noteworthy feature of the reaction with acetone-naphthol is the tendency to form the 3-acyl derivative; thus benzoic anhydride and acetone-naphthol give under certain conditions a 70% yield of 3-benzoyl-naphthoflavone. In each case the unsubstituted chromone was separated from the 3-acyl derivative by tedious fractionation from alcohol.

Naphthopyrone, the parent substance of the series, has been prepared by condensing acetone-naphthol with ethyl formate and sodium and heating the oxymethylene ketone with alcoholic sulphuric acid.

The preparation of a series of chromones derived from 1:3, 1:5, and 1:8-dihydroxynaphthalenes is in progress.

#### 120. $\beta$ -Diketones in ring formation. Part iii.

UMAPRASANNA BASU, Calcutta.

In continuation of a previous work (J. Indian Chem. Soc., 1930, 7, 481) it has now been found that *p*-toluoylacetone gives rise to two different pyridone derivatives when condensed with cyanoacetamide in presence of diethylamine. The main product (about 90 % of the total yield) is 3-cyano-4-methyl-6-(*p*)-tolyl-2-pyridone, m.p. 330-31°, which on hydrolysis



yields 4-methyl-6-(*p*)-tolyl-2-pyridone; the other isomer is 3-cyano-4-(*p*)-tolyl-6-methyl-2-pyridone, and gives 4-(*p*)-tolyl-6-methyl-2-pyridone on hydrolysis.

The O-ether of the above  $\beta$ -diketone,  $\text{CH}_3\text{C}(\text{OEt})=\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3(p)$  was also condensed with cyanoacetamide, when 3-cyano-4-methyl-6-(*p*)-tolyl-2-pyridone was exclusively obtained. This again suggests that the reaction between *p*-toluoylacetone and cyanoacetamide takes place through the enolic form  $\text{CH}_3\text{C}(\text{OH})=\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3(p)$  of the former. Further work with other O-ethers of  $\beta$ -diketones is in progress.

## 121. Synthesis of munjisthin.

P. C. MITTER and HAROGOPAL BISWAS, Calcutta.

2-Chloro-6-methoxytoluene (Ullmann and Panchaud, *Annalen*, 1906, 350, 108) is condensed with phthalic anhydride in presence of aluminium chloride giving 2'-chloro-3'-methyl-4'-methoxybenzoyl-2-benzoic acid. On treatment with sulphuric acid this gives 1-chloro-2-methyl-3-methoxy anthraquinone, which on demethylation gives 1-chloro-2-methyl-3-hydroxy anthraquinone. On oxidation with nitrous acid in presence of boric and sulphuric acids according to the method of D.R.P. 273341, this gives munjisthin.

## 122. Attempts towards the synthesis of nopinone.

P. S. MAYURANATHAN and P. C. GUHA, Bangalore.

The synthesis of a diketo-diester like 1, 1-dimethyl-3, 5-dione-2, 6 cyclohexanedicarboxylic ester was effected by condensing isopropylidene malonic ester with ascetoacetic ester. The bridging of the diketodiester in position 2 and 6 by a methylene group is being tried according to the method of Carl. E. Kerr (*J.A.C.S.* 1929, 51, 614) with the object that the bridged product can be converted into nopinone.

## 123. Studies in the synthesis of higher fatty acids.—Part IV.

P. RAMASWAMI AYYAR and V. A. PATWARDHAN, Bangalore.

(1) The isolation of  $\gamma$ -keto-7-methyloctoic acid (m.p.  $47^\circ$ - $48^\circ$ ) has been effected from the products of the reaction between isoamyl magnesium bromide and succinic anhydride (or methyl ester succinic chloride).

(2) Similarly  $\gamma$ -keto-6-methylheptoic acid (m.p.  $41$ - $42^\circ$ ) has been made by the action of isobutyl magnesium iodide on succinic anhydride.

(3) By the action of an excess ( $2\frac{1}{2}$  mols.) of magnesium ethyl iodide on dimethyl sebacate, a glycol,  $\text{C}_{18}\text{H}_{38}\text{O}_2$  (m.p.  $60^\circ$ ) and a liquid hydroxy acid (equivalent=244) have been prepared.

(4) The action of an excess of magnesium methyl iodide on 11-bromo-undecylic methyl ester has yielded a glycol  $\text{C}_{26}\text{H}_{54}\text{O}_2$  (m.p.  $81^\circ$ ) and a saturated liquid alcohol as the main product.

(5) The action of an excess (3 mols.) of magnesium methyl iodide on methyl laurate gives a quantitative yield of the tertiary alcohol  $\text{C}_{14}\text{H}_{30}\text{O}$  (b.p.  $115$ - $116^\circ/3.5$  mm.).

## 124. An attempted synthesis of allenecarboxylic acid.

B. K. MENON, Bangalore.

Ethoxy methylene benzyl cyanide, prepared by the action of ethyl iodide on oxymethylene benzyl cyanide, was condensed with benzyl cyanide in the presence of ether and sodium. The sodium compound was decomposed and  $\alpha\gamma$ -diphenylglutacononitrile (m.p.  $82^\circ$ ) was obtained. The glutacononitrile was treated with bromine in chloroform solution and



a bromo-compound melting at 126° obtained. Further work in the elimination of hydrobromic acid and the hydrolysis of the resulting nitrile to the carboxylic acid is in progress.

### 125. On the synthesis of uric acid.

M. N. RAMASWAMY and P. C. GUHA, Bangalore.

The present paper is a continuation of previous work (Proc. Ind. Sc. Congress 1930). The stability and method of formation of ring systems containing the -CO- and -NH- groups (which are akin to the polypeptides) have been studied. Phenyl carbonate is a better reagent to introduce a ring forming 'CO' than phosgene as has been found in the case of synthesis of carbo-oxalyldiurea, from oxalyldicarbamide. The possibility of such systems being readily bridged internally has been shown by the ease with which glycolyldicarbamide forms a hydantoin derivative.

### 126. Synthesis of amino-acids.

M. N. RAMASWAMI and S. L. JANNIAH, Bangalore.

The condensation of aromatic aldehydes with acyl derivatives of glycine has been the basis of a useful method for the synthesis of amino-acids like tyrosine, etc. The use of glycine is rendered inconvenient owing to side reactions resulting in the formation of azlactones and of bodies resembling the Schiff's bases. If, however, glycine ester hydrochloride be employed, these complications do not arise. In this case the resulting product exhibits geometrical isomerism (involving a nitrogen with a double bond) which has been studied. The influence of substituents in the glycine molecule on the reaction is being investigated.

### 127. Asymmetric synthesis.

P. NEOGI and Md. ISHAQUE, Calcutta.

(1) Cinnamic acid dibromide.—Dextro and lævo-rotatory varieties were partially obtained on bromination of cinnamic acid, in the presence of quinine and cinchonine and removal of the alkaloids.

Negative results were however obtained in the presence of quinidine, cinchonidine and brucine. Positive results were also obtained with chlorination of cinnamic acid.

(2) Dibromide of cinnannic aldehyde.

Negative results were obtained in the presence of alkaloids and dextrose.

(3) Crotonic acid dibromide.

Negative results were obtained in the presence of alkaloids and sugars

### 128. Transformation of $\omega$ -cyanoacyl amines.

MOHAMMAD ISHAQ and J. N. RAY, Lahore.

$\omega$ -Cyanoacyl amines condense with aromatic ortho-nitroaldehydes and these on reduction pass to  $\alpha\beta$ -substituted quinolines. With ortho-hydroxyaldehydes they give anilido coumarins. Similar transformations to heterocyclic substances are described.

### 129. Synthesis in the Cyanomaclurin series.

J. S. AGGARWAL and J. N. RAY, Lahore.

Coumarins on methylation under strictly regulated conditions pass to o-methoxycoumarinic acids. These are easily reduced to dihydro-deri-



vatives with sodium amalgam. These acids condense with resorcinol to give the corresponding ketones.

A few transformations of these bodies are described.

### 130. 1 : 3 : 4-Triazoles.

K. L. BHAGAT and J. N. RAY, Lahore.

Diacyl hydrazines react with aromatic amines to give 1 : 3 : 4-triazoles. These substances show properties not unlike strychnine. A number of these compounds having properties like strychnine but without action on the rhythmic contraction and toxicity of smooth muscles, are described.

### 131. On the constitution of 2 : 2'-dinitrobenzaldazin.

K. L. BHAGAT and J. N. RAY, Lahore.

*o*-Nitrobenzaldehyde gives with hydrazine a product, m.p. 78° which is transformed to a substance m.p. 204°C. when heated in solution or in the solid state. The probable constitution and mechanism of its formation is now elucidated.

### 132. Experiments in the synthesis of brazilin (VI).

M. ABDUL HAQ and J. N. RAY, Lahore.

$\omega$ -Cyano resacetophenone condenses with veratric aldehyde to give the corresponding  $\alpha \beta$  unsaturated ketone. Experiments are described on the pyrone ring closure of substances of this type.

### 133. Some new hydrocupreidine derivatives.—Part I.

S. GHOSH and N. CHATTERJEE, Calcutta.

The preparations of some hydrocupreidine derivatives were taken up in order to study their pharmacological and biophysical properties, the members of the corresponding isomers, the hydrocupreines, being very active physiologically. Excepting ethyl-hydrocupreidine, which is a known substance, none of the higher homologues have as yet been prepared. As the derivatives of hydrocupreines from the iso-series are more active than the normal compounds, the preparation of the hydrocupreidines of the iso-series were taken up first. The compounds described here are (1) iso-propyl-hydrocupreidine  $C_{22}H_{30}O_2N_2$ , (2) isobutyl-hydrocupreidine  $C_{23}H_{32}O_2N_2$ , (3) Isoamyl-hydrocupreidine  $C_{24}H_{34}O_2N_2$ , and (4) secondary octyl-hydrocupreidine  $C_{27}H_{40}O_2N_2$ .

These derivatives were first prepared like ethyl-hydrocupreidine by the cold-process, viz., by keeping a mixture of potassium hydrocupreidine and the alkyl iodide in absolute alcohol at room temperature for about a month. We modified the process as follows: The potassium compound of hydrocupreidine was dissolved in absolute alcohol, treated with the alkyl iodide and a small amount of molecular copper as catalyst and heated on the water-bath under reflux for about 2½ hours. The separation of the base was done as usual. The yield of this modified process was in most cases better than by the cold-process and there was considerable economy of time.

### 134. Organo-antimony compounds.—Part V.

S. C. NITYOGY, Calcutta.

In a previous communication (J. Indian Chem. Soc. 1930, 7, 577), it has been found that stibinic acids derived from aminobenzylbenzoates and benzylaminobenzoates are without any marked action in the



treatment of Kala-azar. So far as is known, it appears that the presence of an amino-group together with a stibinic acid grouping is essential for the production of an active trypanocide. A series of compounds is now being studied containing both the above groupings.

### 135. Quinoline stibinic acids.

R. N. SEN *and* G. MUKHERJI, Calcutta.

With a view to study the properties and the therapeutic value of the antimony compounds of quinoline, in which the antimony atom occupies the ortho, meta and para positions to the quinoline-nitrogen atom, the corresponding diazotised ortho-, meta-, and para-aminoquinolines have been treated with antimony chloride solution and the addition products decomposed with cold caustic alkalis, when the sodium salts of quinoline-stibinic acids are formed. The ortho- and para-quinoline-stibinic acids have been isolated in the pure state. The therapeutic values of these compounds are under investigation.

### 136. Aromatic di- and poly- stibinic acids.

S. M. MISTRY *and* P. C. GUHA, Bangalore.

By following the method of D.R.P. 261,825, a distibinic acid has been obtained from 1 : 4-naphthylene-diamine as also from p : p-diaminostilbene. By slightly altering the experimental conditions a di-stibinous oxide is obtained from p-diaminostilbene to the complete exclusion of the distibinic acid. Tri-stibinic acids have been obtained from sym-m-triamino-triphenyl-phosphine, sym.-m-triaminotriphenyl-arsine and sym. m-triamino-triphenyl-stibine.

### 137. Introduction of arsenic in Coumarine Neucleus.

M. N. GOSWAMI *and* H. N. DAS GUPTA, Calcutta.

With a view to prepare coumarine-arsenic acid 6-aminocoumarine was submitted to Bart's reaction. The product obtained was a light yellow solid after crystallisation from acetic acid. It decomposes at 226°C and dissolves in alkali to dark brown solution. On analysis it was found that it contained about 14% arsenic which shows that the compound is tricoumarine-arsenic oxide instead of coumarine-arsenic acid. Bart's reaction was modified by taking a solution of arsenic trichloride in hydrochloric acid solution instead of the usual mixture of sodium carbonate and arsenious oxide and the reaction was conducted in acid media. Identical product was obtained. The practical advantage of this modification appears to be that the formation of tar and tremendous frothing attending the Bart's reaction are entirely avoided. Roeder and Blase method of the synthesis of phenylarsenic acid was applied to Coumarin mercuric chloride with a view to prepare the Coumarin-arsenic acid but it was found that in contact with arsenic trichloride Coumarin mercuric chloride suffered entire decomposition. Coumarin mercuric chloride used in this experiment was prepared by the method of Roeder and Blase as applied in the preparation of phenyl mercuric chloride and the authors do not find any justification for the limitations in its preparation as set forth by Sen and Chakrabarty (J.I.C. Soc. 1929).

Further experiments regarding the introduction of arsenic in other Coumarins and Naphthacoumarins are in progress.



## 138. A new method of preparing mercury derivatives of organic compounds. Part II.

P. NEOGI and MD. ISHAQUE, Calcutta.

P. Neogi and S. Neogi (J.C.S. 1927, 131, 30) showed that the period of induction in the interaction of mercuric chloride and sodium bicarbonate is greatly enhanced in the presence of glycerol. Advantage has been taken of this phenomenon by Neogi and Chatterjee (J.I.C.S., 1928) in developing a method of preparing mercury derivatives of organic compounds. Nayak and co-workers, with the authors' permission, have applied this method to the preparation of mercury compounds of malonamide and its derivatives. In this paper the method has been applied to the preparation of mercury derivatives of thymol, o-, m-, and p-toluidine,  $\alpha$ - and  $\beta$ -naphthylamine,  $\alpha$ - and  $\beta$ -naphthol. Carvacrol gives no compound thus showing the influence of some groups in the benzene nucleus on the reaction.

## 139. New methods of preparation of Halogenomercuri phenols.

V. V. NADKARNY, Bombay.

Mercuration of phenol by mercuric chloride in the presence of a small quantity of NaOH has been effected. A mixture of monohalogeno-compounds was obtained. (This method differs from those used by Desesquelle, and P. Neogy; the former used a phenolate and then the composition of the compound obtained is not established. Neogy using  $\text{NaHCO}_3$  and glycerol,—obtains a compound which on double decomposition with NaCl gives the required halogeno derivative).

Also phenol has been mercurated by mercuri-acetamide. This method has given a general mode of preparation which applies not only to all the mono-halogeno (i.e., fluoro, chloro, bromo, iodo,) but also to the di-halogeno mercuri derivatives of phenol.

## 140. On lignoceric acid from the seeds of adenanthera pavonina. Part II.

P. RAMASWAMI AYYAR, Bangalore.

In continuation of work previously described (see Proc. Ind. Sc. Congress 1928, p. 161) the following new derivatives have been prepared: *Methyl ester*, ( $\text{C}_{25}\text{H}_{50}\text{O}_2$  m.p.  $58^\circ$ ); *Lignoceryl alcohol*, ( $\text{C}_{24}\text{H}_{50}\text{O}$  m.p.  $72-73^\circ$ ); *Lignoceryl iodide*, ( $\text{C}_{24}\text{H}_{50}\text{I}$  m.p.  $49-50^\circ$ ); *Lignocerane*, ( $\text{C}_{24}\text{H}_{50}$  m.p.  $51-52^\circ$ ); *Iodo-acid*, ( $\text{C}_{24}\text{H}_{47}\text{IO}_2$  m.p.  $74-75^\circ$ ); *Hydroxy-acid*, ( $\text{C}_{24}\text{H}_{48}\text{O}_3$  m.p.  $94-95^\circ$ ); *Methoxy-acid*, ( $\text{C}_{25}\text{H}_{50}\text{O}_3$  m.p.  $61-62^\circ$ ); and *Isotricosanic acid* by degradation ( $\text{C}_{23}\text{H}_{46}\text{O}_2$  m.p.  $73-74^\circ$ ).

The work is being continued.

## 141. Oxidation of "Embelin" with nitric acid.

D. B. LIMAYE and G. R. GOGTE, Poona.

The results of Hefter and Feuerstein regarding the oxidation of "Embelin" were recently contradicted by Kaul, Roy, and Dutt (Proc. Ind. Sc. Congress, 1929, 148), who isolated pelargonic acid as against lauric acid by the former authors. As one of us had observed the formation of lauric acid by the action of nitric acid on "Vidangin" (Proc. Ind. Sc. Congress, 1926, 151), a substance closely related to "Embelin", and isolated from the berries of "Embelia Ribes", the action of nitric acid on "Embelin" itself was studied.

In all experiments an acid melting at  $43.5^\circ\text{C}$ , and identical with the ordinary lauric acid to which normal structure has been assigned, was isolated along with lauronitrile and lauramide.



In a later publication, however, Kaul, Roy, and Dutt (*J. Ind. Chem. Soc.* 1929, VI, 577) do not refer to their having isolated pelargonic acid, but mention a new acid—isolauric acid—melting between 33° and 35°C, as obtained by the action of nitric acid on "Embelin". In view of our results we doubt the formation and the individuality of their isolauric acid, and confirm the results of Hefter and Feuerstein.

#### 142. $\Delta^3$ Carene.

B. SANJIVA RAO and G. A. SREENIVASAN, Bangalore.

$\Delta^3$  Carene nitrosate has been separated into two modifications by repeated fractional crystallisation. The action of bases on the nitrosate has been studied. Results of oxidation of carene with benzoyl-hydroperoxide are described.

#### 143. Studies in optical rotation. Part II.

S. M. MISTRY, S. M. PATEL, and P. C. GUHA, Bangalore.

By condensing 1 : 4-naphthylene-diamine with p-acetyl-amino-benzaldehyde, a compound was obtained which after hydrolysis of the acetyl groups was condensed with camphor-quinone. The compound, obtained, viz., 1 : 4-naphthylene-bis-iminobenzylidene-bis-imino-camphor, (m.p. 239°C) contains 17 double bonds and shows the highest optical

rotation recorded as yet  $\left[ M \right]_{5780}^{25^\circ} = 22049.9^\circ$ .

#### 144. Studies in optical rotation.

S. M. MISTRY and P. C. GUHA, Bangalore.

The following compounds have been prepared for condensation with camphorquinone :—

- (a) pp-diaminodinaphthyl-urea.
- (b) pp-diaminodiphenyl-hydrazodicarbonamide.
- (c) pp-diaminodiphenyl-azodicarbonamide.
- (d) pp-diaminodiphenyl-glyoxal.
- (e) pp-diaminoazobenzene.
- (f) pp-diaminohydrazobenzene.
- (g) pp-diaminobenzil.
- (h) 1 : 4-diaminoanthracene.

pp-Diaminobenzophenone and the free amine obtained by the hydrolysis of the condensation product between anthraquinone and acetyl-p-phenylene-diamine, do not condense with camphorquinone.

Further experiments are in progress.

#### 145. Studies on phototropism in solution. Part III.

B. SINGH and B. BHADURI, Cuttack.

This work is a continuation of that already described (*J. Amer. Chem. Soc.*, 1921, 43, 333 ; *Journ. Ind. Chem. Soc.*, 1924, 1, 45).

A chloroform solution of  $\alpha$ -naphthylamino-d-camphor turns green in sunlight. The change is accompanied by marked acidity of the green solution. It is further found that the phototropic change is also brought about in bromoform as well as in a solution of ethyl alcohol containing iodoform.

On the other hand, a solution of the substance in the following halogenated solvents does not exhibit phototropy :—carbon tetrachloride, ethyl iodide, and ethylene dibromide.

Sodium ethoxide as well as a trace of water inhibit the phototropic change.



The rotatory power of chloroform solution of  $\alpha$ -naphthylamino camphor *before* and *immediately after* exposure is the same. It increases gradually on keeping the solution in the dark, although the green colour of the solution is discharged and replaced by yellow. The rotatory power in bromoform solution of the substance is very slightly affected, and it is not affected at all in an alcoholic solution in the presence of iodoform on exposure, although the original colourless solution changes to green and then to yellow.

$\alpha$ -naphthylaminocamphor on acetylation loses its phototropic behaviour.

146. Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part X. The Rotatory Dispersion of Stereoisomeric (a) Aryl Derivatives of Imino and Amino-Camphor and (b) Camphorquinones.

B. SINGH and H. P. BASU-MALLIC, Cuttack.

In this paper the condensation products of aniline, o-, m- and p-iodo-aniline with camphorquinones (d-, l-, dl-) and their reduction products are described.

O-iodophenyliminocamphor occurs in three forms. These are shown to be polymorphic and not isomeric by the method already described (Singh, *Journ. Ind. Chem. Soc.* 1929, 6, 1007). The rotatory dispersion of these compounds are determined for four wave-lengths, namely, NaD 5893, Hg<sub>yell</sub> 5780, Hg<sub>gr</sub> 5461, and Hg<sub>vio</sub> 4358.

In several cases the rotatory dispersion is found to be "simple", for example, o-iodophenylaminocamphors (except in ethyl alcohol), camphorquinones, and the remaining substances in some solvents.

The rotatory power of the dextro- and laevo- isomerides are identical within the limits of experimental error. These substances further support the assumption of the physical identity of enantiomers as regards their optical rotatory power.

147. Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XI. Stereoisomeric oo'-stilbenebisamino-, and bisaminocamphors; oo'-stilbenebisaminomethylenecamphors; oo'-Dibenzylbisimino- and bisamino-camphors; and oo'-Dibenzylbisaminomethylenecamphors.

B. K. SINGH and B. BHADURI, Cuttack.

oo'-Diaminostilbene (*trans.*) and oo'-diaminodibenzyl are condensed with the three stereoisomeric camphorquinones and oxymethylene camphors. The bisiminocamphor derivatives are reduced in the usual way.

The aryl derivatives of bisaminomethylenecamphors have higher rotatory power than the corresponding ones from bisamino-camphors, but lower than those derived from bisiminocamphors. It is, however, curious that the rotatory power of oo'-dibenzylbis-iminocamphor is higher than that of oo'-stilbenebisiminocamphor, although the conjugation in the former compound is broken.

The rotatory dispersion of these compounds is determined in six solvents for nine wavelengths (from 6708 to 4880 Å) at 35°. In every case except oo'-dibenzylbisaminocamphor, the rotatory dispersion is found to be "simple", i.e., it can be expressed by the one-term equation of Drude,  $[\alpha] = \pm k/\lambda^2 - \lambda_0^2$ .

According to Pasteur's principle of molecular dissymmetry the d- and l- forms are represented as true mirror images of one another, differing in sign, but absolutely identical in all their numerical properties.



The remarkable agreement in the numerical values of the dispersion data for the dextro and laevo enantiomerides now presented, furnishes still further evidence in the correctness of this fundamental assumption.

148. Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XII. The Rotatory Dispersion of Stereoisomeric Aryl Derivatives of Aminomethylenecamphors.

B. K. SINGH, TARAPRASAD BARAT, and BHUTNATH BHADURI, Cuttack.

The condensation products of oxymethylenecamphors (d-, l-, and dl-) with aromatic monamines, e.g. aniline, m-toluidine, p-toluidine,  $\alpha$ -naphthylamine and  $\beta$ -naphthylamine are described.  $\alpha$ -naphthylamine gives two forms which appear to be polymorphic.

The rotatory dispersion is determined for six solvents and eight wavelengths at 35°. In all cases the dispersion is found to be "simple" and it can be expressed by the one-term equation of Drude,  $[\alpha] = \pm k/(\lambda^2 - \lambda_0^2)$ .

The rotatory power of the dextro and laevo isomerides is identical, i.e. it can be expressed by the same equation.

149. Attempts to elucidate the constitution of plumbagio.

NATHU RAM and K. VENKATARAMAN.

Plumbagin, the essential constituent of *Plumbago rosea*, *P. europea*, etc., has been shown by Madinaveitia and Gallego (1928) to be a methyl hydroxy-naphthaquinone. From the analogy of Lapachol, the yellow pigment from the wood of the Lapacho tree, which has been shown by Hooker (*J.C.S.* 1896) to be 2- $\gamma$ - $\gamma$ -dimethyl-allyl-3-hydroxy- $\alpha$ -naphthaquinone. Fieser (*J.Amer.C. S.*, 1927) has prepared Lapachol by heating the O-alkyl ether of 2-hydroxy- $\alpha$ -naphthaquinone. We are synthesising both the naphthaquinones by the interaction of phenyl acetyl chloride with the appropriate alkyl malonic ester: treatment with sulphuric acid would lead to a tetra-hydronaphthalene carboxylic ester. Hydrolysis of the ester and decarboxylation would give an alkyl naphthoresorcinol which on oxidation, would give the desired alkyl hydroxy naphthaquinone.

150. The Constitution of Alkanin. Part II.

M. V. BETRABET and G. C. CHAKRAVARTI, Bangalore.

Further experiments support the molecular formula,  $C_{30}H_{28}O_8$  suggested for alkanin previously (Proc. Ind. Sci. Congress, 1930). On bromination by different methods alkanin yields three distinct bromoderivatives,  $C_{30}H_{26}O_8Br_2$ ,  $C_{30}H_{24}O_8Br_4$  and  $C_{30}H_{22}O_8Br_6$ ; and tetraacetylalkanin yields a tetrabromoderivative,  $C_{30}H_{20}O_8(CO.CH_3)_4Br_4$ . Benzoylation produces the tetrabenzoyl derivative,  $C_{30}H_{24}O_8(CO.C_6H_5)_4$ . The carbethoxy derivative has the composition,  $C_{30}H_{28}O_8(COOC_2H_5)_2$  and the barium compound corresponds to the formula,  $(C_{30}H_{27}O_8)_2Ba$ .

Acetylation and benzoylation of dimethoxyalkanin yield dimethoxydiacetyl alkanin,  $C_{30}H_{24}O_8(OCH_3)_2(CO.CH_3)_2$  and dimethoxy dibenzoyl alkanin,  $C_{30}H_{24}O_8(OCH_3)_2(CO.C_6H_5)_2$  respectively. The observed molecular weights of some simple derivatives of alkanin are in close agreement with their formulæ.

151. The pigments of Tecoma flowers.

C. V. RAMASWAMI AYYAR and K. VENKATARAMAN, Lahore.

The isolation of two flavone pigments from the yellow flowers of *Tecoma glauca*, a common herbaceous plant in Bangalore, is described.



152. The pigments of the flowers of *Poinciana regia*.

C. V. RAMASWAMI AYYAR and K. VENKATARAMAN, Lahore.

The bright red flowers of the Gold Mohur tree were dried at room temperature in vacuum and extracted with 2% methyl alcoholic hydrochloric acid. The anthocyanin pigments were precipitated by ether and partly purified by two repetitions of the same process. The crystallisation of the scarlet flakes thus obtained was effected by the methods of Willstätter and of Karrer. The reactions and properties of the anthocyanin and of the anthocyanidin obtained by hydrolysis are described.

From the ethereal residues a flavone, identified as quercetin, was isolated. It was precipitated as the lead salt, which was then hydrolysed with boiling dilute sulphuric acid. The flavonol was converted into its hydrobromide and the product of hydrolysis was crystallised from aqueous acetic acid (cf. A.G. Perkin, Chem. Soc. Proc., 1914, 30, 177).

## 153. Bhadravati wood tar.

Y. K. RAGHUNATHA RAO and B. S. RAO, Bangalore.

The constituents of the tar were determined by fractional distillation and solvent extraction. Distillation decreases the quantity of alkali-soluble constituents owing to decomposition. The following constituents of the tar have been identified and in some cases quantitatively estimated:—Ortho, meta and para cresol, xylenols, ethyl phenol, guaicol, creosol, coerulignol and pyrogallol ether. The unusual presence of a resorcinol derivative is also indicated. Other constituents are pyridine and its homologues, several ethers, hydrocarbons and acids.

The alkali-soluble portion was divided into 10 fractions by distillation under reduced pressure and the phenol coefficient of each fraction determined. The values varied from 3 to 12 reaching a maximum at the 9th fraction.

Cracking of the tar at atmospheric pressure at 500°C gave an increase in the amount of phenolic bodies.

## 154. The estimation of acetone in methyl alcohol.

S. D. SUNAWALA and M. C. T. KATTI, Bangalore.

Messinger's method for the estimation of acetone was found unsatisfactory in presence of methyl alcohol although the standard conditions suggested by Goodwin were observed. (*J.A.C.S.*, 42, 1920, 39–45). Methyl alcohol was found to become oxidised to formic acid by the hypoiodite, the rate of the reaction diminishing with time owing to the simultaneous oxidation of hypoiodite to iodate. The formation of iodate from hypoiodite was found to be a bimolecular reaction. The method suggested by Scott-Wilson involving precipitation with mercuric cyanide was found to give quantitative results both in methyl and ethyl alcohol solutions, amounts as small as 0.01 mg. being capable of detection.

## 155. The molecular organic compounds of 1 : 3 dichlor 4 : 6 dinitrobenzene.

H. S. JOIS and B. L. MANJUNATH, Bangalore.

The formation of the molecular organic compounds of 1 : 3 dichlor 4 : 6 dinitrobenzene with naphthalene,  $\alpha$ -naphthol and  $\beta$ -naphthol has been observed by means of the cooling curves of mixtures of the components. The compounds with naphthalene and  $\alpha$ -naphthol could be crystallised pure from benzene. But that with  $\beta$ -naphthol could not be crystallised from the usual solvents as it dissociated during the process.



156. *o*-Dinitrobenzene as an impurity in *m*-dinitrobenzene.

P. K. BOSE, Calcutta.

The presence of traces of *o*-dinitrobenzene in *m*-dinitrobenzene (prepared from nitrobenzene) may be shown by the violet colour which develops when a warm alcoholic solution of *m*-dinitrobenzene is successively treated with liquor ammonia and a little sulphuretted hydrogen.

157. *o*-Dinitrobenzene as an analytical reagent.—Part I. A delicate test for reducing sugars.

P. K. BOSE, Calcutta.

On heating a mixture of *o*-dinitrobenzene, a reducing sugar and an alkali solution, a beautiful violet colour is developed. The reaction is not given by non-reducing carbohydrates. The limit of detectability is one drop of 0.025% in 2 c.c. of solution in the case of glucose and most other reducing sugars.

158. *o*-Dinitrobenzene as an analytical reagent.—Part II.

P. K. BOSE, Calcutta.

A polyhydric phenol having at least two OH- groups in the ortho : or para- position to one another gives a violet or purple colour with *o*-dinitrobenzene in alkaline solution. Meta- derivatives give negative results. This test might be used with advantage for the location of OH- groups in natural products of unknown constitution.

159. *o*-Dinitrobenzene as an analytical reagent.—Part III.

P. K. BOSE, Calcutta.

Sulphuretted hydrogen, even in minute quantities, gives a violet colour with a warm alcoholic solution of *o*-dinitrobenzene in presence of ammonia or alkali. The action of various sulphur compounds on aromatic ortho-dinitro-compounds is being studied.

## 160. Phthalazines.—Part III.

J. S. AGGARWAL, I. D. KHERA, and J. N. RAY, Lahore.

Extension of the work of Aggarwal, Darbari, and Ray has now led to the synthesis of phthalazine analogues of papaverine. These substances are hydrolysed by alcoholic hydrochloric acid and phthalic anhydride to aldehydo-ketones of the aromatic series. A number of these hydrolytic products are now described.  $\alpha$  acyl  $\beta$  alkyl hydrazines give almost quantitative precipitation of copper complexes. These are being explored for a rapid method for estimation of copper.

## 161. Attempts to find Anti-malarials.—Part VI.

K. S. NARANG and J. N. RAY, Lahore.

Azlactones derived from *o*-nitrobenzaldehydes and hippuric acid give iminazolones when treated with aromatic amines and Cu powder. These on reduction pass to quinolino-iminazoles. These substances have a part of their structure derived from quinine and the iminazole part being partly analogous to harmala group of alkaloids, it is expected that they will be of value in sub-tertian malaria. This is being investigated jointly with Prof. Hesse of Breslau.



162. Synthesis of Triazines: Action of aminoguanidine on orthodiketones.

S. C. DE and P. C. DUTT, Muzaffarpur.

The communication deals with the preparation and properties of some triazine derivatives obtained by the condensation of aminoguanidine with the various derivatives of acenaphthoquinone and isatin, such as 1-nitro and 3:4-dinitro acenaphthoquinones, bromoisatin, dibromoisatin, chloroisatin, dichloroisatin, nitroisatin, etc., with a view to study the effects produced on the colour of the triazines by the introduction of different elements or groups of elements. The triazines thus obtained dye wool in various shades ranging from yellow to reddish brown.

163. Complex pyrodiazolones.—Part I.

T. N. GHOSH and M. V. BETRABET, Bangalore.

Andreocci (Gazetta, 1889, 19, 448) obtained a pyrodiazolone by condensing acetylurethane with phenylhydrazine. From the reaction mixture he isolated, besides the pyrodiazolone, another crystalline compound whose constitution he could not definitely establish. Acetylurethane has now been condensed with phenylhydrazine, p-nitrophenylhydrazine etc. under different experimental conditions and in each case a mixture of an amidine which does not form any azo-derivative and a pyrodiazolone derivative has been obtained. By condensing the pyrodiazolone which contains the (-NH-CO-) grouping, with anthranilic acid, a mixture of carboxy-phenylimino-pyrodiazolone and pyrodiazolone-4:5-quinazoline derivatives has been obtained. Acetylurethane reacts with thiosemicarbazide and its substitution products to yield, in each case, two compounds, viz.—a hydrazo-amidine compound which gives an azo-derivative on oxidation with ferric chlorides and the corresponding pyrodiazolone compound.

164. Isomeric imino-thiobiazolones and imino-thiol-thiobiazoles.—Part III.

S. L. JANNIAH and P. C. GUHA, Bangalore.

Besides the isomeric compounds isolated before (Ind. Sci. Congress Abs. 1929, p. 21, No. 67), the phenyl and tolyl substituted hydrazo-dithio-dicarbonamides have also been found to exist in two different isomeric forms and to yield isomeric compounds on ring closure. Thus the acetyl derivative (m.p. 224°) of diphenylhydrazodithio-dicarbonamide (m.p. 187°) gives on hydrolysis with hydrochloric acid of different concentrations two isomeric compounds melting at 249° and 208° the former obtained also from the hydrazide by treating directly with concentrated acid. The ditolyl hydrazide behaves in a similar way. The consideration of these results and the absorption spectra curves suggest a similarity in structure between the new compounds obtained by hydrolysis and endoxy-amino-thiobiazole.

165. Isomerism in the triazole series.

S. L. JANNIAH and P. C. GUHA, Bangalore.

3:5-Dithiol-1:2:4-triazole (m.p. 196°) gives an acetyl derivative, m.p. 330°, which on hydrolysis, instead of giving back the original compound yields a compound, m.p. 228°, which is isomeric with the dithiol triazole. Similar cases of isomerism is being studied with other 4-N-substituted dithiol triazoles. 3:5-Aminothiol-1:2:4-triazole on acetylation and subsequent hydrolysis gives back the parent compound.



## 166. Complex quinazolines.

P. K. BOSE *and* OTHERS, Calcutta.

Heterocyclic compounds containing the system  $-N=C(Cl)-$  in the ring readily condense with anthranilic acid forming complex quinazolones. On treatment with alkali the quinazolone ring opens up and the carboxylic acid thus obtained reverts to the original quinazolone by the action of heat or suitable dehydrating agents.

## 167. Di-aldehydo-phenolphthalein.

R. N. SEN *and* K. C. KAR, Calcutta.

Phenolphthalein gave a mono-aldehyde (J. Indian Chem. Soc., 1929, 6, 53-63.) by the application of Reimer and Tiemann's reaction in an alkaline solution, in which it presumably exists in a quinonoid configuration with only one phenolic group active. With a view to preparing the corresponding di-aldehyde, phenolphthalein has been first reduced with zinc dust in an alkaline solution (Annalen, 202, 36-140) and the reduced product in caustic soda solution has been treated with a mixture of alcohol and chloroform (4 : 1), added slowly with constant stirring at  $50^{\circ}$ - $60^{\circ}$  C. The di-aldehyde, thus obtained, when crystallised from dilute alcohol, is a slightly yellowish crystalline substance (fine needles) softening at  $234^{\circ}$  C and decomposing at  $237^{\circ}$  C to an amber coloured liquid. It gives a bisulphite compound, a di-oxime, a di-semicarbazone, and a di-phenylhydrazine. It reduces ammoniacal silver nitrate solution, giving a beautiful mirror, but it does not reduce Fehling's solution. It dissolves in ammonia, sodium-bicarbonate, sodium-carbonate and caustic soda solution, giving colourless solution in all cases. The alkaline solution, if allowed to stand exposed to air gradually turns pink. The aldehyde is oxidised by atmospheric oxygen and more readily by alkaline potassium ferricyanide into di-aldehydo-phenolphthalein which is under investigation.

## 168. The cyanine dyes.

M. Q. DOJA, Patna.

A general survey has been made of all the published work on the subject, ample references to the original papers being provided. In the review special attention has been paid to the more chemical side of the problem. The paper ends with a reference to some interesting points which still await investigation.

## 169. A handy manometer for the organo-chemical laboratory.

M. Q. DOJA, Patna.

The setting up of a small direct reading and fairly accurate manometer has been fully described. Diagrams are also given wherever necessary.

## 170. Di-Salicylaldehyde and dyes derived from it.

R. N. SEN *and* S. DUTT.

Di-salicylaldehyde or 4 : 4'-dihydroxy-3 : 3'-dialdehydo-diphenyl melting at  $185^{\circ}$  C has been prepared by Reimer and Tiemann's reaction on *p-p*-dihydroxy-diphenyl with a yield of about 50% using chloroform mixed with alcohol. It gives a di-phenylhydrazine, a dioxime, a di-semicarbazone and a dibenzoyl derivative. It undergoes benzoin condensation and reacts with acetone in an alkaline medium.

Di-Salicylaldehyde produces interesting dyes—(1) azo-methine dyes—by its condensation with mono and diamines (ring compounds being obtained in the case of ortho and para phenylene diamines), (2) Pyronine dyes—



by condensation with resorcinol, pyrogallol and diethyl-m-aminophenol,  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) being used as condensing agent, (3) triphenyl methane dyes when condensed with dimethyl aniline and ortho cresotinic acid.

The resorcinol compound produces an orange shade on silk and wool (octabromo derivative—a red shade), the pyrogallol compound black and green shades on iron—and chromium-mordanted wool respectively, the compound with o-cresotinic acid yellowish-red shades on aluminium- and chromium-mordanted wool, the dimethyl aniline compound a green shade and di-ethyl-m-amino-phenol compound a violet shade on silk, wool and tannin-mordanted cotton.

### 171. Dyes derived from thiohydantoin.

G. P. PENDSE and S. DUTT.

Thiohydantoin has been found to condense readily with aromatic nitroso and isonitroso compounds in presence of acetic anhydride to form deep coloured compounds which dye cotton and wool from an alkaline bath. The reaction takes place between the nitroso group and the methylene group of thiohydantoin. The products are crystallised from pyridine or glacial acetic acid.

### 172. Dyes derived from Acenaphthenequinone : azines, azonium, and anilino compounds.

S. K. GUHA, Patna.

In continuation of the work of Sircar and Guha (*J. Chem. Soc.*, 1924, 125, 335) this paper further describes the comparison of the tinctorial properties of certain azine and azonium derivatives with those of the corresponding Phenanthraquinone derivatives. (Sircar and Dutt, *J. Chem. Soc.*, 1922, 121, 1944), (Dutt, *J. Chem. Soc.*, 1922, 121, 1951). The following compounds have been prepared: 3-Chloroacenaphthaphenazine, 3-Chloroacenaphthatholazine, 3-Bromoacenaphthatholazine, 3-Chloroacenaphthanaphthazine, 3-Bromoacenaphthanaphthazine, 3-Chloroacenaphthaphenazine, 3-Bromoacenaphthaphenazine, Phenyl-3-Chloroacenaphthanaphthazonium nitrate, Phenyl 3-Bromoacenaphthanaphthazonium nitrate.

These compounds are all well-defined crystalline substances, characterised by high melting point. They dissolve in concentrated sulphuric acid with a characteristic colour from which water precipitates the original substances as flocculent mass and well adapted for dyeing (from an acid bath). Their dyeing shades on wool are quite even and vary from yellow to reddish brown.

Mukherjee and Watson (*J. Chem. Soc.*, 1916, 109, 625), Sircar and Dutt (Loc. Cit.), and Dutt (Loc. Cit.) have shown that Bromine atom is replaced by Ullman's method (Ber., 1901 34, 2174) in the Phenanthraquinone series, giving rise to anilino compounds which are deeper in colour. Anticipating the same to happen in the Acenaphthenequinone series the author applying Ullman's reaction got 3-anilino-acenaphthenequinone and 3-anilino-acenaphthaphenazine from the corresponding bromo compounds. They are amorphous black coloured substances. Further work in this direction is in progress.

### 173. 1-Aldehydo-2-oxy anthraquinone and dyes derived from it.

R. N. SEN and S. ROY, Calcutta.

An alcoholic solution of chloroform (3:1) reacts with 2-oxy-anthraquinone in aqueous alkaline solution on the boiling water bath producing 25% ortho aldehyde; microcrystalline powder from nitrobenzene, melting



above 300°. (Tri-semicarbazone, also does not melt below 300°C). The aldehyde condenses with dimethyl-aniline, in the presence of hydrochloric acid, and with resorcinol, ortho cresotinic acid and diethyl-m-aminophenol in the presence of concentrated Sulphuric acid to produce interesting dyes. The C=O groups in the anthraquinone ring do not react in these condensations. The oxidised dimethyl-aniline compound, dyes silk and wool blue and greenish-blue shades, the diethyl-m-aminophenol compound producing a reddish-violet shade, and the resorcinol compound an orange shade; the ortho-cresotinic acid compound, on oxidation with nitrosyl-sulphate, dyes wool a yellow shade which changes to reddish-brown by after-chroming.

#### 174. Dyes obtained from phenanthraquinone.

S. C. DE and P. C. DUTTA, Muzzaffarpore.

In continuation of the work of Sircar and Dutta (*J. Ind. Chem. Soc.*, 1924, 1, 201) the present investigation was undertaken with a view to study the effects produced on the colour of the monoazines by the introduction of an additional chromophoric azine ring in positions adjacent to each other. A number of quinoxalophenanthrazines have been prepared and their colours have been compared with those of the monoazine derivatives—such as phenanthraphenazines and phenanthranaphthazines and with those of the phenanthraphenazinazines having two azine rings connected through a benzene nucleus and it has been found that the quinoxalophenanthrazines have got deeper colour than those of the corresponding monoazines but have lighter shades than those of the phenanthraphenazinazines.

#### 175. A new synthesis of Crystal Violet.

R. N. SEN and ASHUTOSH MUKHERJI, Calcutta.

Crystal Violet has been successfully synthesised, in high yield, by a new method, namely, by bringing about a condensation between excess of carbon tetrachloride and dimethyl aniline in the presence of anhydrous aluminium chloride, as in Friedel and Craft's reaction. It is necessary to moderate the reaction, in the beginning by cooling, after which it is carried out at room temperature for some time, and is finally finished on the water bath.

The work is in line with Hofmann's synthesis of Fuchsine from carbon tetrachloride and aniline, and with the condensations of chloroform, carbon tetrachloride and iodoform with resorcin and other aromatic hydroxy compounds. (Sen, Sinha, and Sarkar, *J.I.C.S.*, 1, 303, 1925.)

Similar other condensations with chloroform and carbon tetrachloride are in progress.

#### 176. 5 and 7-aldehydo-8-oxyquinolines and dyes derived from them.

R. N. SEN and S. ROY.

An alkaline solution of 8-oxyquinoline when heated on the water bath with a mixture of alcohol and chloroform (3 : 1) gives 16% 7-aldehydo-8-oxyquinoline, reddish microcrystalline powder melting above 250° (phenylhydrazine melting at 143° and 30% 5-aldehydo-8-oxyquinoline melting above 250° (phenylhydrazine, m.p 120°); the ortho compound giving a deep greenish-yellow tinge with Ferric chloride while the para compound producing a faint yellowish colouration.

The aldehydes have been condensed with dimethyl anilin and resorcinol in the presence of concentrated hydrochloric acid and with ortho-cresotinic acid in the presence of concentrated sulphuric acid to produce triphenyl-methane dyes. Pyronine dyes have been obtained by condensing the



aldehydes with (1) diethyl-m-amino-phenol and (2) resorcinol in presence of sulphuric acid. The oxidised dimethylaniline compounds dye wool and silk a deep blue shade and the oxidised ortho cresotinic acid compounds dye a beautiful orange shade; the diethyl m-amino-phenol compounds producing a reddish-violet shade. The resorcinol compounds when the pyrone ring is not closed (when condensed with Concentrated hydrochloric acid) dye silk and wool a golden yellow shade, while by closing the pyrone ring (when condensed with Concentrated Sulphuric acid) the compounds produce a reddish orange shade.

### 177. Studies on Pyronine dyes.

R. N. SEN and S. SINHA.

No convenient method is known at present by which Rosamines could be obtained in one stage by the condensation of benzaldehyde with dimethyl-m-aminophenol. It has now been observed that an aldehyde condenses with dimethyl-m-aminophenol producing Rosamine dyes with pyrone ring formation in one stage and with good yield in the presence of concentrated sulphuric acid at 160–190°, which acts both as a dehydrating and an oxidising agent.

With a view to determine whether the reaction admits of a general application and also to study the influence of the nature and position of certain groups in the aldehyde molecule on the colour and fluorescence of such pyronine dyes, dimethyl-m-aminophenol has been condensed with Benzaldehyde, ortho-, meta-, and para nitrobenzaldehydes, meta and para-aminobenzaldehydes, dimethyl-p-aminobenzaldehyde, ortho, meta-, and para hydroxy benzaldehydes, anisaldehyde, Vanillin, Meta and para chloro benzaldehydes,  $\beta$ -Naphthol aldehyde, Furfural, cinnamic aldehyde and paraldehyde. The reactivity of the Substituted benzaldehydes is generally much greater than that of benzaldehyde and the substituent in the meta position generally increases the reactivity of the aldehyde more than the ortho and para substituents; of all the aldehydes investigated, furfural is the most reactive, the reaction taking place at about 130°C. The influence of the ortho and para substituents on the colour and fluorescence of these compounds is generally much greater than that of the meta substituents; the nitro and the hydroxy compounds are much bluer than the unsubstituted compounds. The nitro group completely destroys the fluorescence.

### 178. Tetraphenyl methane dyes. Part II.

R. N. SEN and M. GHOSH.

Sen and Banerjee (*Proc. Ind. Sc. Congress*, 1929) obtained Tetraphenylmethane dyes by condensing rosaniline base with aromatic amino and hydroxy compounds. Similar dyes have been now obtained by condensing (1) crystal violet base and (2) malachite green base with aromatic amino and hydroxy compounds in the presence of fused sodium acetate at 160–180°C with a yield of 60 to 80%. They are as good dyes as the triphenyl methane dyes though they do not contain any ordinary chromophore and do not admit of a quinonoid configuration according to the usually accepted mode of tautomerisation.

The compounds derived from the crystal violet or the malachite green base may be regarded as the base, in which the carbinol 'O H' has been replaced by a phenyl residue with or without any auxochromic group, and their colour is generally similar to that of the parent base more or less modified by the additional auxochromic groups. The condensations of crystal violet and malachite green bases with the following amino and hydroxy compounds have been studied; aniline, dimethyl aniline, phenol, anisol, resorcinol, resorcinol dimethylether and methyl salicylate.



## 179. Attempts to prepare dyes from fluorenone.

A. C. SIRCAR and K. C. BHATTACHARYYA, Calcutta.

Ring structure, with its compact arrangements of double linkages, promotes absorption in the visible part of the spectrum, *i.e.*, produces colour. This is markedly demonstrated in the case of fluorenone which is deep yellow, whilst benzophenone is absolutely colourless. Again the ortho-diketone benzil is only yellow, whilst the corresponding closed ring ortho-diketone phenanthraquinone is orange red.

That the colour of such ring-structured compounds can be further deepened by the introduction of groups in the nucleus has been shown by Watson and his collaborators.

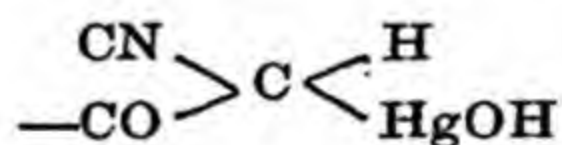
The object of the present investigation was to prepare dyes from fluorenone in the same way as has been done from benzophenone on the one hand and phenanthraquinone on the other. A good number of dyes has now been prepared from fluorenone. They are described in the paper. A new derivative of fluorenone, *viz.*, 2-iodo-fluorenone has also been prepared.

## 180. Mercury acetamide as a mercurating agent.

K. G. NAIK and L. D. SHAH, Baroda.

Mercury Acetamide has been systematically used for the first time for the preparation of organo-mercury compounds. The following compounds were investigated:—(1) Cyanacetmethylamide, (2) Cyanacetethylamide, (3) Cyanacetpropylamide, (4) Cyanacetbutylamide, (5) Cyanacetamylamide, (6) Cyanacetiso-hexylamide, (7) Cyanacetiso-butylamide, (8) Cyanacetheptylamide, (9) Cyanaceticester, (10) Cyanacetamide, (11) Cyanacetanilide, (12, 13, 14) Cyanacet o-m-and p-tolylamides, (15) Cyanacet benzylamide, (16) Cyanacet  $\alpha$ -naphthylamide, (17) Cyanacet  $\beta$ -naphthylamide, (18) Cyanacet Xylidide, (1 : 3 : 4) (19) Cyanacet Xylidide, (1 : 4 : 5).

By the interaction of these amides with mercury acetamide in dilute alcoholic solution, the hydroxy-mercury derivatives of the general constitution



were obtained.

The properties of these mercury derivatives indicate the presence of a very weak C-Hg bond such as is always found when the carbon involved is alpha to a carboxyl or a carbonyl group. The actions of hydrochloric acid, hydrogen sulphide, potassium iodide, phenyl hydrazine, etc., have been studied which indicate the presence of a very weak C-Hg bond in these compounds.

181. The interaction of metallic sodium with compounds containing a reactive methylene ( $\text{CH}_2$ -)group.

K. G. NAIK and L. D. SHAH, Baroda.

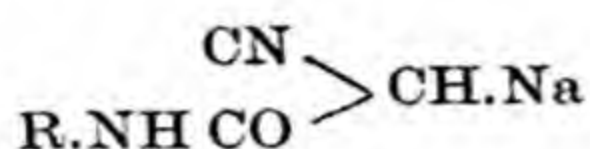
An attempt has been made to study the reactivity of the hydrogen atoms of a reactive methylene ( $\text{CH}_2$ -) group, by studying the case of formation of the sodio derivatives of a number of substituted Cyanoacetamides. During these investigations one of the negative groups ( $\text{CN}$ -) was common to all compounds and the negativity of the other group was slowly altered.

The following substances were examined:—

- (1) Cyanacet m-toluidide, (2) Cyanacet o-toluidide, (3) Cyanacet p-toluidide, (4) Cyanacetbenzylamide, (5) Cyanacet  $\alpha$ -naphthylamide, (6) Cyanacet  $\beta$ -naphthylamide, (7) Cyanacetic



ester, (8) Cyanacetamide, (9) Cyanacetmethylamide, (10) Cyanacetbutylamide, (11) Cyanacet heptylamide. In all the above cases only mono-substituted derivatives of the general constitution



were generally obtained.

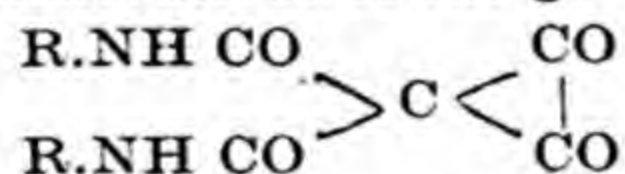
The results of these investigations afford clear evidence that the interaction of metallic sodium with compounds containing a reactive Methylene ( $\text{CH}_2$ -) group depends largely on the electronegative character of the attached groups.

### 182. Interactions of oxalyl chloride with substances containing a reactive Methylene ( $\text{CH}_2$ -) group.

K. G. NAIK and P. N. DESAI, Baroda.

The present investigations were undertaken with a view to study the reactivity of the two hydrogen atoms of the reactive Methylene group. The interaction of Oxalyl Chloride with the following substances was investigated.

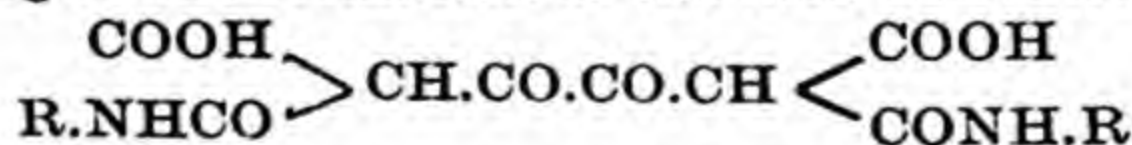
(1) Malondi-p-tolylamide, (2) Malondi-m-tolylamide, (3) Malondi-o-tolylamide, (4) Malondi- $\alpha$ -naphthylamide, (5) Malondi- $\beta$ -naphthylamide, (6) Malondi-phenylamide, (7) Malondi-benzylamide, (8) Malondi-methylphenylamide, (9) Acetoacetanilide, (10) Ethyl malonp-tolylamate, (11) Ethyl malon o-tolylamate, (12) Ethyl malon  $\alpha$ -naphthylamate, (13) Ethyl malon Xylilamate, (1: 3: 4) (14) Ethyl malon Xylilamate, (1: 4: 5:) (15) Ethyl malon phenylamate. Two types of compounds were obtained; Type I. Compounds (1) to (6) react with Oxalyl Chloride yielding the cyclopropane derivatives of the general constitution



Type II. compounds (6) to (9) react with Oxalyl Chloride to give open chain compounds of the type



In the case of compounds (10) to (15) the hydrolysis of the ester group takes place leading to the formation of the acid derivatives:—



It was also found that the reactivity of the hydrogens of a methylene group is influenced in much the same way by the adjacent groupings as was found by Naik and his other collaborators.

### 183. The unsaturation and tautomeric mobility of heterocyclic compounds of the thiazole type in relation to modern electronic conceptions.

R. F. HUNTER, Aligarh.

In this paper, the following problems have been investigated:—

- (i) The lability of the unshared electrons of the nuclear nitrogen atom in benzthiazole derivatives.
- (ii) The reversion of N-dibromides containing singlet linkages, to the conventional ammonium ion structure.



- (iii) The isolation of a series of stable N-dibromides which are analogues of the pentahalides of P, As, and Sb.
- (iv) The effect of fluorine and iodine substituents on the tautomeric mobility of semi-cyclic amidines.
- (v) The unsaturation and tautomeric mobility of simple mono-nuclear thiazole compounds.

The whole field of the earlier work has been revised in the light of modern electronics and evidence is adduced for the operation of a *lone singlet* linkage in certain special cases of polybromide ion formation.

#### 184. Active principles from *Solanum Xanthocarpum*.

D. D. KANGA, Ahmedabad.

This drug which is common throughout India is "much esteemed as an expectorant and is used in cough, asthma, catarrhal fever and pain in the chest." Its vernacular name is Bhuringni (Bombay).

Fruits were examined separately as well as the whole plant.

A Gluco-alkaloid is found in the fruits. On hydrolysis with acid it gives a crystalline alkaloid (M.P. 174–75°C) and a sugar which is yet to be identified. The alkaloid gives an insoluble hydro-chloride. Another crystalline substance (shining plates) is obtained from the petroleum ether extract of the crude drug with a M.P. 245°C (sharp).

*Whole plant:* The same gluco-alkaloid is found here also. The crystalline substance (M.P. 245°C) mentioned above is not found here but a green crystalline substance, apparently homogeneous, is obtained from the alcoholic extract. This is found to be a complex substance giving tests for a chloride, a nitrate, potassium, a trace of iron and more than one organic substance. From the aqueous extract potassium chloride (cubes), and potassium nitrate (long flat needles) crystallize out.

The investigation of both the drugs is proceeding.

#### 185. Geometrical inversion in light.

B. K. VAIDYA, Liverpool.

1. Quantum efficiency determinations for the inversion of the following geometrical isomers have been made: maleic and fumaric acids; citraconic acid; o-coumaric acid, cinnamic and isocinnamic acids. The mean respective values are: 0.048, 0.117, 0.182, 0.030, 0.609, and 0.206, for the wave length  $313\mu\mu$ , with slight variations depending on the concentration of the solution.

2. It is suggested that in substances showing selective absorption, the quantum efficiency value would approach unity as the exciting radiation decreases in wave length, within one of the *photochemically active bands*. As far as the present work is concerned the substances showing general absorption, or those in which the exciting radiation fails to fall within an active band, appear to have a low quantum efficiency.

3. Measurements on the velocity of inversion of cinnamic and isocinnamic acids which totally absorb the incident energy show them to belong to the zero order reaction.

4. Possible reasons for the inactivity of mesaconic acid and crotonic acid are discussed.

#### 186. Raman effect in some geometrical isomers.

B. K. VAIDYA, Liverpool.

1. Raman spectra for methyl acetate and dimethyl esters of maleic, fumaric, citraconic, and mesaconic acids (two pairs of geometrical isomers) have been obtained on a large Littrow model spectrograph giving high dispersion.



2. The difference between a *cis* and a *trans* molecule is noticed in the lower absorption frequencies corresponding to regions of long wavelengths  $13\text{--}16\mu$  and  $32\text{--}35\mu$ . This is probably the result of the difference in the molecular rotational frequencies of the two molecules.

3. As the *cis* and the *trans* molecules possess similar groups and linkings, the higher absorption frequencies which originate from various chemical bonds are the same in both the molecules. All these frequencies have been identified with definite chemical bonds.

### 187. Condensation of butyl chloral with gallic acid and the three cresotic acid.

A. N. MELDRUM and B. N. KATRAK, Bombay.

The present investigation was undertaken with a view to compare the behaviour of butyl chloral with that of chloral in condensation with the benzene nucleus. Using sulphuric acid as condensing agent (as used with chloral) butyl chloral has been condensed with hydroxy and methoxy benzoic acids.

1. (a) 1 Molecule of butyl chloral and one of acid give a phthalide (gallic, trimethoxy benzoic and syringic acids).

(b) 4 Molecules of butyl chloral and one of gallic acid give a compound containing the phthalide ring and a heterocyclic ring.

2. (a) Butyl chloral and the cresotic acids in presence of hydrochloric acid combine in the proportion of 1 : 1.

(b) Butyl chloral and the cresotic acids combine in the proportion of 1 : 2.

Generally chloral and butyl chloral behave in a similar way in these condensations : there are minor divergencies in behaviour.

### 188. Investigation of the method of differential dialysis, with special application to the separation of the digestion products of the proteins.

S. V. DESAI, Pusa.

The preliminary portion of the work has been devoted to the study of the dialysis of simple chemical substances. The separation of these is shown to be possible by differential dialysis using membranes of graded permeability prepared under certain standard conditions. The differential dialysis of starch solution yielded fractions which gave different colouration with iodine.

The differential dialysis of commercial peptone through a particular series of graded membranes gave fractions which agreed fairly closely with the fractions obtained by salt and other precipitation methods. The distribution of nitrogen in these fractions showed a progressive increase in the ratio of amino to peptide nitrogen as the fractions became more complex.

Proteolytic digests were prepared from Gelatin, Egg albumin, Fibrin (blood), Glutelin (wheat), and Casein.

The degree of digestion by pepsin was different in each case, and in general was higher than had been previously recorded. The non-amino nitrogen of the digest corresponded to that computed from the distribution of nitrogen of the corresponding protein estimated by acid hydrolysis, showing a resemblance between pepsin hydrolysis and acid hydrolysis.

The maximum digestion of gelatin by trypsin showed the extent to which hydrolysis is possible by this enzyme, again the amount of digestion was much higher than that recorded by previous workers. The main point of interest is that the nitrogen of the digest which is not converted into amino nitrogen after acid hydrolysis is considerably



greater than in the case of gelatin or its pepsic digest. Thus the non-amino nitrogen content appeared to be greatly increased by tryptic digestion.

The differential dialysis of the digests through a series of graded membranes gave fractions which differed from each other in nitrogen distribution. Excepting in some fractions of irregular composition the ratio of amino to peptide nitrogen increased as the fractions themselves became less readily dialysable. The distribution of non-amino nitrogen was more striking. Apart from the simple non-amino nitrogen (chiefly ammonia) which readily dialyses out with the simpler split-products, the non-amino nitrogen appears to be concentrated in the most complex fractions of all, suggesting the presence of either the "arginine nuclei" of Kossel or the pre-existence of ring structures in the protein molecule.

#### 189. Mechanism of phytosynthesis of proteins in plants.

K. S. VARADACHAR, Bangalore.

This problem which has baffled all previous workers is sought to be attacked, by feeding the nutrient-nitrate, asparagine, ammonium salts or amino acids through the stem with the aid of a hypodermic syringe needle. The method of injection consists in fixing a hypodermic syringe needle diagonally in the stem and attaching a reservoir of the solution to the needle so that the injection is done slowly under hydrostatic pressure.

The plants (*Helianthus annuus*) which have been raised in glazed pots on sand containing all nutrients except nitrogen respond readily to the treatment. They are being collected at definite intervals and examined for the distribution of nitrogen in various forms. Results of considerable interest have already been obtained.

#### 190. Investigations on some cell-wall constituents of plants.

H. S. SHARMA, Bangalore.

Lignified tissues like those of teak, and pine yield high percentages of lignin and hemicelluloses and low ones of pectin, while nonlignified tissues like those of turnip, radish and palm fruit yield the reverse.

Pectin exists in the cell-wall as mono-methylated and tri-methylated pectic acid and there are indications of the former being isolated. The hemicelluloses vary in the percentages of their constituents depending largely on the nature and the process of metabolism of the plant concerned.

Attempts are being made to trace the exact nature of the changes, Pectin  $\rightarrow$  Hemicellulose  $\rightarrow$  lignin and Pectin  $\rightarrow$  Sugars  $\rightarrow$  Alcohols.

Attempts are being made to arrest the change at the pectin stage, so as to help preservation of fruits. In the case of vegetables, the completion of the change culminating in lignification at ripening may not be of much food value and the use of such vegetables at the pectin and hemicellulose stage is desirable.

Pectin readily undergoes decarboxylation on treatment with weak alkalis. Thus treatment with 0.5% alkali yields products similar to hemicelluloses which contain smaller percentages of uronic acid and resist further decarboxylation. A quantitative study of the change from pectin to hemicelluloses is being attempted.

#### 191. Preparation and properties of fish-gelatin.

H. JAI RAM, Bangalore.

Gelatin obtained from fish-skins was purified by electrolytic methods and freed from mucin, condriotin, etc.

Fish-gelatin did not separate as a pure flocculum in acid, alkaline or neutral media. The purified product consisted mainly of the soluble



form and behaved like heated animal gelatin or soluble *ana*-gelatin obtained by the *an*-ionic flocculation of bone gelatin in alkaline media.

The gelatin is not readily precipitated by salt solutions. On addition of ammonium sulphate although the precipitation commences at 35% saturation, it is complete only at 90–95%. It is, however, completely precipitated by alcohol or acetone.

Osmotic pressure measurements show that the gelatin is a complex protein with a high molecular weight.

There is no temperature "lag" in the viscosity of this gelatin and the viscosity remains practically unaltered on heating.

There was no increase in the basic fractions as a result of treatment with acids in the cold showing a similarity with *ana*-gelatin in that no *dl*-lysine is produced under such conditions.

## 192. The basic hydrolysis products of fish-gelatin.

H. JAI RAM, Bangalore.

The basic hydrolysis products of fish-gelatin were examined in detail. In addition to arginine, histidine and lysine, the basic fraction of fish-gelatin contained oxy-lysine,  $\text{CH}_2(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$ , which was isolated by Kingston and Schryver's carbamate method. "Protoctine" could not be found in the hydrolysis products. There is indication to show that this gelatin contains minute quantities of a hitherto undescribed base which is extractable with absolute alcohol from the lysine fraction. This base reduces an acid solution of potassium permanganate, is easily soluble in alcohol and water. It is exceedingly hygroscopic.

## 193. Influence of electrical treatment on enzymes present in seeds.

K. VENKATAGIRI, Bangalore.

Passage of alternating current (210 V, 0.15 amp.) for about 1 hour through salt solution in which barley is soaked and subsequent germination leads to preparation of a malt having 40% more diastatic power than that obtained from the same barley without electrical treatment.

The increased activity is not due to adsorption of either the whole salt or one of the ions. A preparation of the enzyme obtained by dialysis of the extract from treated malt is more active than a similar one from untreated malt. The treated malt contains less protein than the untreated one.

Lipase in resting castor seed does not respond to electrical stimulation.

## 194. Studies in enzyme action.—Part V. 'Thermoresistance' of papain.

N. DESIKACHAR, Bangalore.

Papain which is soluble in water is not, by itself, thermoresistant. It is however able to withstand even the temperature of boiling water when present together with freshly coagulated papaya latex which is mostly protein. Means of preserving this valuable property in commercial preparations are being studied.

## 195. Studies in enzyme action.—Part IV. The nature of the coagulating ferment in papaya milk.

N. DESIKACHAR, Bangalore.

As in the case of blood, the coagulation can be hastened by addition



of calcium salts and retarded or stopped in presence of oxalate. The chemical and the biological changes involved in the above and the allied phenomena have been discussed.

196. Power alcohol from papayas previously lanced to milk papain.

N. DESIKACHAR, Bangalore.

Papaya fruit contains a large amount (67% on the dry weight) of sugar. Almost all the sugar is easily extracted with water by cooking at 30 lbs. pressure for 15 minutes.

Fermentation trials carried out with 5 different strains of yeasts showed that *S. Jorgensen* gave the best yields, 98% of the sugar being converted into its equivalent of alcohol. Additions of ammonium and potassium phosphates hastened the rate of fermentation and helped to secure the high yield cited above.

A conservative estimate shows that it will pay to raise papayas even if it is merely for the manufacture of industrial alcohol. The fruits are obtainable at practically all the seasons of the year, the sugars easily extracted, and the fermentation carried out in a short space of time.

The taste and the flavour of the fermented product suggest that the liquor may find favour at least among certain sections of people as an alcoholic beverage.

197. Dilatometric studies in enzyme action.—Part II. Urease and arginase.

H. B. SREERANGACHAR and M. SREENIVASAYA, Bangalore.

The enzymic hydrolysis of urea and arginine has been followed by the dilatometric method (*Science Congress Proceedings*, 1927, 14, 171; *Biochem. J.*, 1929, 23, 975). In the case of urease the contraction is so great that even with 1 mm. bore capillary the course of hydrolysis can easily be followed. The applicability of this method to the estimation of urea in physiological liquids is indicated.

198. Amylase from wheat.

D. V. KARMARKAR and V. N. PATWARDHAN, Bangalore.

Amylase from germinated wheat is found to be more active than that from barley malt. The enzyme from ungerminated wheat has no liquifying action. The optimum temperature of wheat-malt-amylase lies between 49° and 58°; the optimum reaction is PH 4.6. The dry amylase loses its activity if heated for one hour at 160°. The enzyme undergoes an irreversible loss of activity on prolonged dialysis. Pepsin inactivates the enzyme.

199. Amylase from rice.

D. V. KARMARKAR and V. N. PATWARDHAN, Bangalore.

Amylase from germinated rice is found to have activity equal to that from barley malt. The optimum temperature is 60°C. and the optimum reaction, PH 4.7. The enzyme undergoes loss of activity on dialysis as well as on standing. Pepsin has no action on the enzyme. Further work is proceeding.

200. Physico-chemical studies on enzymes : Amylase.

K. VENKATAGIRI, Bangalore.

Physical and physico-chemical factors associated with the activation and the determination of amylase under different conditions have been studied.



## 201. Inactivation of Castor seed lipase.

S. N. GODBOLE and D. R. PARANJPE, Nagpur.

Different oils were hydrolysed by Tannaka's castor-seed-lipase method. But the locally obtained oil from Indian black mustard seeds showed this phenomenon. The mustard oil obtained by petrol extraction shows normal hydrolysis. The Bonducella oil obtained from the seeds by pressure also showed inactivation. Both these oils contain sulphur glucoside. Sulphur glucoside from Bonducella added to any normal oil also inhibits the hydrolysis. Probably oils contaminated with glucosides containing sulphur show this effect.

## 202. Estimation of maltose in plant extracts by maltase.

N. NARASIMHAMURTY and M. SREENIVASAYA, Bangalore.

A reliable method for the estimation of maltose in mixtures of sugars occurring in plant extracts and tissue fluids has been described wherein an enzyme extract rich in both maltase and invertase has been used as the hydrolysing agent. The method is selective in its action and completely eliminates the errors inherent to the method of acid hydrolysis.

203. An investigation of the alcohol extract of Fenugreek.  
(*Trigonellum Foenum-Graecum*).

M. SREENIVASAYA, B. N. SASTRY, and Y. V. SRINIVASA RAO, Bangalore.

The white amorphous body which separates on addition of acetone to the alcohol extract referred to in the last year's communication has been fractionated into pyridine soluble and pyridine insoluble portions the latter being rich in sulphur. The pyridine soluble portion has been fractionated further by successive additions of chloroform, resulting in four precipitates which were purified by dissolving in alcohol and precipitating by acetone. All the fractions are optically active, the last fraction being definitely laevo rotatory ( $-21.5^\circ$ ). Acid hydrolysis of each of the fractions results in the liberation of a reducing sugar which has been identified as galactose. Experiments point to the conclusion that the pyridine soluble portion consists of a mixture of two galacto-lipins, the dextro lipin occurring in a higher proportion.

204. Chemical constituents of the root bark of *Plumbago Rosea*.

V. N. PATWARDHAN and M. C. TUMMINKATTI, Bangalore.

The alcoholic extract of the powdered root bark was extracted with petrol-ether, ether, chloroform, ethyl-acetate, acetone and alcohol. Plumbagin, the presence of which was reported by one of us (M. C. Tumminkatti) at the Calcutta Meeting, was all extracted by petrol-ether and ether. Besides plumbagin, the fatty material contained in the petrol-ether and ether extracts is being examined. It contains sitosterol (m.p.  $135^\circ$ — $136^\circ$ ). Chloroform, ethyl acetate and acetone extracts yield nothing definite. Glucose was identified in the alcoholic extract. Further work is being carried out.

205. The constitution of the active principle of *Corchorus Capsularis*, Part II.

N. SEN, Dacca.

Corchoritin, a new non-glucosidic bitter substance, m.p.  $218$ – $220$ , has been isolated from jute-seeds and in all probability has the composition



$C_{12}H_{18}O_3$ . The formation of a monoacetate m.p.  $120-122^\circ$  and a phenylurethane compound m.p.  $254-256^\circ$ , establishes the presence of a hydroxyl group. It contains no aldehydic or ketonic carbonyl grouping and no free carboxyl group but the presence of a lactonic grouping is shown by the slow titration of the solution with aqueous alkali hydroxide in presence of phenolphthaleine (neutralisation value =  $0.84$ ; sap. value =  $196.2$ ). The alcohol is unsaturated and reacts with bromine (Iodine value =  $136.6$ ). Treatment of corchoritin in alcoholic solution with dilute sulphuric acid yields a yellow compound,  $C_{10}H_{14}O_2$  m.p.  $97^\circ$ , which on distillation with zinc dust gives a white sublimate, which has a naphthalene-like smell and yields a red picrate but it has not been definitely characterised. Oxidation with nitric acid yields a nitro compound, succinic acid, oxalic acid and carbonic acid whereas treatment with permanganate leads to a ketocarboxylic acid which gives a positive iodoform reaction with alkaline iodine solution and therefore must contain  $—CO.CH_3$  group.

Corchoritin, therefore, appears to contain two hydrogenated rings in the molecule and is closely related chemically to corchogenin,  $C_{16}H_{26}O_3$ —the hydrolysed product of the glucoside Corchorin described in Part I (*Ind. Sc. Congress*, 1930).

## 206. Alcoholysis of cocoanut oil.

M. N. GOSWAMI and S. RAMANUJAM, Calcutta.

The simultaneous hydrolysis and esterification of fatty acids liberated have been tried by means of catalysts other than Hydrochloric Acid. The following have been used:—

- (i) Phosphorous Oxychloride; (ii) Benzene Oleo-Sulphonic Acid;
- (iii) Naphthalene Oleo-Sulphonic Acid; (iv) Piperidine;
- (v) Piperidine Hydrochloride; (vi) Pyridine.

In each case the same amounts of oil, methyl alcohol, ether and the catalysts were used. Comparative experiments with Hydrochloric Acid were also done under similar circumstances. It was observed that of all the catalysts used Phosphorous Oxychloride came next to Hydrochloric Acid in giving good results.

Detailed experiments are in progress.

## 207. A Method for the determination of the saponification value of highly coloured oil.

H. S. JOIS, B. L. MANJUNATH, and S. VENKATARAO, Bangalore.

It was observed during the course of some investigation on highly coloured oils that the usual method of determining the saponification value failed, as the end point with phenolphthalein could not be accurately gauged. The electrometric methods of determining the end points can only be used when suitable apparatus is available. It was found, for this purpose, that the Albert method for the determination of the acid number of dark coloured resins as modified by Coburn (*Industrial and Engineering Chemistry. Analytical Edition* 181, 2, 1930) could be applied with very satisfactory results. The method also holds good for the determination of the acid numbers of coloured oils and mixed acids in the regular oil analysis.

## 208. The saponification of emulsified oils. Part—I. A new method for the determination of the degree of emulsification.

P. C. SPEERS and R. L. GUPTA, Lahore.

During the course of the study of the saponification of emulsified oils, it was found that there is a definite break in the electrometric titration



curve of a particular emulsion, and that this break is different for different emulsions. It was, therefore, felt that this may be utilised as one of the methods for determining the extent of emulsification of the oils. Experiments were carried out in this direction and the results obtained were compared with the e.m.f.s. developed as a result of the Thomson Thermoelectric Effect and the comparison was quite satisfactory. Efforts are still being made in this direction to examine the sensitivity of the method.

## 209. Chemical examination of the roots of *Hygrophylla Spinosa*.

N. N. GHATAK and S. DUTT, Allahabad.

*Hygrophylla Spinosa* of the natural order of Acanthaceae is a plant growing in marshy places throughout India. The roots, seeds and leaves are widely used in Indian medicine. The chemical examination of the root led to the isolation of a new phytosterol  $C_{28}H_{46}O$  having a melting point at  $193^{\circ}$ . The phytosterol has a specific rotation  $(\alpha)_D^{30} = 27.8^{\circ}$ .

Henry (J., 1920, 119, 1624) claims to have isolated a phytosterol of the same molecular formula, but melting at  $265^{\circ}$ . He holds this compound as an exception to the other members of this family in its acetyl derivative having a lower melting point than that of the parent substance, and also in its being laevorotatory. So apparently the phytosterol isolated by Henry is quite different from the phytosterol of the present authors. The acetyl derivative of the present compound melts at  $206^{\circ}$ .

A yellow oil, a light green wax and a large amount of maltose have also been obtained from the roots. A bromo derivative and a digitonide have been prepared from the phytosterol. By the action of thionyl chloride a crystalline chloro derivative was obtained, but it was found to contain sulphur as well.

## 210. Investigation of the dried rind of the fruit of *Garcinia Gambogia*.

K. I. KURIYAN and K. C. PANDYA, Agra.

*Garcinia Gambogia* is a small evergreen tree of the Western coast and Ceylon. Among other things it gives an edible fruit of a pleasant acid taste. The dried rind of the fruit is extensively used as a condiment and is eaten with fish as a substitute for tamarind, in Cochin, Travancore, and South Malabar. In Travancore it is known as KODUMPULI in Malayalam. In appearance it has some resemblance to the fruit of *Garcinia Indica*, or kokum, a better known member of the same family.

While the acid principle in tamarind has been well investigated by Sudborough and Vrindhachalan, the authors are not aware of any work done on *Garcinia gambogia*.

The rind of the fruits was obtained from Kottayam (South India) and indicated the presence of free acid and salts, including iron, calcium, magnesium, sodium, potassium, tartaric acid, citric acid, phosphoric acid and reducing sugars.

The quantitative results were :

Free acid: 100 grams of the dried rind required 11.45 grams of NaOH.

Tartaric acid: Percentage of potassium hydrogen tartrate 13.6, corresponding to 10.6 % tartaric acid.

Phosphoric acid: determined as calcium triphosphate 1.52 %.

Reducing sugars calculated as glucose :

aqueous extract	gave	7.4 %.
acid	" "	15.2 %.
alkali	" "	14.8 %.



Thus the amount of tartaric acid present is much less than in tamarind, and as the tree is less abundant than tamarind, it can be thought of still less as a commercial source of the supply of tartaric acid.

211. Examination of the fruit-pulp of *Parkia Biglandulosa* (Black Pods), Part I.

P. RAMASWAMI AYYAR and V. A. PATWARDHAN, Bangalore.

The whitish pulp yields to methyl alcohol 20 per cent. of a syrupy liquid. The latter after being freed from a small percentage of saponin by means of lead acetate shows in a 30 per cent. aqueous solution an  $[\alpha]_D = + 33^\circ$  but very slight reduction towards Fehling's solution. After hydrolysis with dilute acid the  $[\alpha]_D$  changes to  $+ 12^\circ$  in a 5 per cent. aqueous solution and it further yields an osazone melting at  $203^\circ$ , besides showing considerable reduction with Fehling's solution. Further work is in progress.

212. The occurrence of carvacrol.

JAGJIT SINGH and B. SANJIVA RAO, Bangalore.

The oil from *Thymus serpyllum* has been found to contain carvacrol (42%), trace of thymol, p-cymene, terpinene, linalol, borneol and caryophyllene.

213. Formation of curcumone.

N. C. KELKAR and B. SANJIVA RAO, Bangalore.

Experiments on the formation of curcumone from curcuma oil are described (Rupe, Ber. 1910, 42, 2515). During this investigation a more complete investigation of the curcuma oil has also been made and it has been found to contain  $\alpha$ -phellandrene, cineol, borneol, zingiberene, and sesquiterpene alcohols.

214. Chrysalis oil from Mysore silkworms.

P. RAMASWAMI AYYAR and V. C. PAREKH, Bangalore.

The chrysalids yielded to petroleum ether 20.4 per cent. of a clear reddish-brown oil which had the following analytical characteristics:

Sp. gr. $25^\circ/25^\circ$	=	0.9208
$n_{\frac{27^\circ}{D}}$ ..	=	1.4742
Acid value ..	=	18.7
Saponification value	=	202.0
Iodine value ..	=	117.6

The composition of the fatty acids is being studied.

215. Oil from the seeds of *moringa pterygosperma* (Gärt).

P. RAMASWAMI AYYAR and V. C. PAREKH, Bangalore.

The seeds of which a bitter variety was procured from Kathiawar contained 65 per cent kernels and 35 per cent. husks. The kernels yielded to petrol 26.6 per cent of a clear yellow oil, which has the following characteristics:—

Sp. gr. $33^\circ/28^\circ$	=	0.9022
$n_{\frac{27^\circ}{D}}$ ..	=	1.4638



Acid value ..	=	17.9
Saponification value	=	183.3
Iodine value ..	=	65.0
Unsaponifiable matter	=	3.7 per cent.

The mixed acids freed from unsaponifiable matter gave the following analytical data :

Mean molecular weight	=	303.6
Iodine value ..	=	65.3
Unsaturated acids	=	73.3

The composition of the fatty acids is being studied.

## 216. Investigation of the oil of Undi (*Calophyllum inophyllum*).

H. W. PATWARDHAN, Nagpur.

The oil was procured from Ratnagiri. The oil is used as an illuminant in those parts. It has a dark greenish colour and a peculiar odour. On analysis the following constants for the oil were obtained:—

Acid value ..	..	24.6
Saponification value		204.0
Iodine value ..	..	102.0
Hehner number		92.3%
Unsaponifiable matter	..	1.7%
Refractive index	..	1.4775 at 28°C.
Specific gravity	..	0.932
Acetyl value ..	..	24.8

The fatty acid from the ether extracted soap has a dirty green colour and furnishes the following constants:—

Mean molecular Wt.	..	294
Iodine value ..	..	104.0

The saturated and the unsaturated acids were separated by Twichell's lead-salt-alcohol method. The percentages of the saturated and the unsaturated acids were 23.7 and 75.3 respectively. The mean molecular Wt. of the saturated acids is 350. The unsaturated acids gave 136 as the iodine number and 281 as the mean molecular Wt.

The oil was hardened in the presence of nickel pumice catalyst and the hydrogenation was seen to progress normally.

Further work is being carried on.

## 217. A study of Niger seed oil *Guizotia abyssinica*

N. P. KALE, Poona.

The cold pressed oil, golden yellow in colour, is a drying oil, I.V 126. 4; S. V. 196.7.

The composition of the insoluble fatty acids:—

Unsaturated acids	..	..	85.4%
containing-Oleic	..	36.4%	
a-modification of Linolic		46.7%	
other modifications of Linolic		16.9%	
Saturated acids	..	..	14.6%
containing-Myristic and Lauric		2.5%	
Palmitic	..	61.8%	
Stearic	..	33.2%	
Arachidic and Lignoceric		2.4%	
On bromination the oil gave			
Tri-linoleate	..	..	2 to 2.4%
Di-lino-oleo	..	..	20 to 22%
Other mixed glycerides	..	..	The rest



The fresh oil on exposure to air thickened slowly as a result of hydrolysis and oxidation, with the formation of anhydrides or lactones. The oil dried in 12 to 18 hours when treated with driers. When thickened by blowing with oxygen at higher temperatures, peroxides and ketones or aldehydes were formed.

The oil in the seed at various stages of formation after fertilisation showed an increase in the iodine value and decrease in the saponification value and acid value. At the earlier stages, reducing sugars were found in appreciable quantities which went on decreasing and at last vanished when the seed is fully developed. Starch could not be detected at any stage of the development of the seed though other carbohydrates and proteids were found to accumulate to a certain stage and then to decrease to a slight extent.

## 218. Investigation of the oil from Baheda seeds (*Terminalia belerica*).

J. G. SHRIKHANDE and S. N. GODBOLE, Nagpur.

The oil was extracted with petrol-ether. It had a brownish-yellow colour and a characteristic odour. The following are the constants for the oil :—

Percentage of the oil	..	..	..	42%
Sp. gravity	..	..	..	·9093
Refractive index at 27·8° c.	..	..	..	1·464
Saponification value	..	..	..	181
Iodine value	..	..	..	97
Acetyl value	..	..	..	23·72
Unsaponifiable matter	..	..	..	1·5%
Hehner value	..	..	..	92%
Acid value	..	..	..	Nil

The fatty acids from the ether extracted soap have a brownish-yellow colour and gave the following constants :—

Mean molar weight	..	..	..	285
Iodine value of the mixed fatty acids	..	..	..	98

The percentages of the saturated and unsaturated fatty acids were 39 and 60 respectively.

Mean molar weight of the saturated acids	..	282
Mean molar weight of the liquid acids	..	279–280.

## 219. Parkia Oil.

D. R. PARANJPE, Nagpur.

The oil is obtained by extraction from the crushed seeds of *Parkia biglandulosa* legumes. Petrol ether extraction gives 16·5% yield of a pale yellow oil, solidifying between 10° and 15°. The saponification value is 189·5; iodine value 80·87; specific gravity ·9209 at 15°; refr. ind. 1·4705 at 21·2°; Reichert Meissel value 1·2; Polensky value ·25; Hehner number 94·7 and unsaponifiable matter, 1·11. The oil has no acetyl value. The mixed fatty acids from the dry soap have mean molar weight 290·2; iodine value 81·8; titre 39·5; saturated acids 59·77% and unsaturated acids 40·0% (Twitchel). The mean molar weight of liquid acids was 283 and iodine value 134·8; refr. ind. ·4582 at 45°. The absence of hexabromides leaves only the oleic and linolic acids, the proportion for which works out at oleic:linolic = 43·70:56·30 which is confirmed from the bromination products. The m.p. of tetrabromide separated is 113°. The saturated acids possess mean molar weight 288·0; refr. ind. 1·4370 at 65° and gives titre test 53·5°. The fractional distillation and subsequent



examination of the methyl esters of saturated acids gave the composition of saturated acids as palmitic : stearic : behenic as 40.46 : 61.15 : 36.30 in 138 gms. of mixture. Thus the composition of the original mixed fatty acids of the oil works out as palmitic 8.8%, stearic 13.3%, behenic 7.9%, oleic 30.6% and linolic 39.4%. The unsaponifiable matter has a characteristic odour and the digitonin reaction gave 21.22% sterols. The peculiarity with this oil is that while it contains a fair amount of the higher saturated acid like behenic acid, it also contains a large proportion of linolic acid which is a regular deviation from the composition of most of the normal oils.

220. Examination of the chemical constituents of *Withania Somnifera*.

D. N. MAJUMDAR and P. C. GUHA, Bangalore.

A reducing sugar, phytosterol, ipuranol, mixture of saturated and unsaturated acids and a small quantity of a basic substance, supposed to be an alkaloid, have been isolated.

221. Studies on the effect of heat treatment on lac.

M. VENUGOPALAN and M. RANGASWAMI, Ranchi.

Effect of heating lac at different temperatures and for different lengths of time has been tried with the view of evolving a shellac with a higher softening point but without an appreciable deterioration in the properties of the natural product, notably the fusibility and the solubility in alcohol.

Optimum conditions of heating have been found for both higher and lower temperatures and the results obtained so far indicate that heating at 100° for three hours and at 110° for two hours seem to give the best results. In these experiments the melting point is raised by about 10 degrees above the normal without at the same time affecting its solubility.

Viscosities of 10 per cent solutions of all the samples are increased as the result of heating. This is supposed to be due to greater aggregation of the shellac molecules either in solid state or in dispersed condition.

The acid and iodine values have not undergone any marked change except exhibiting a slight decrease or increase in these values with rise in temperature.

Shellac films obtained from the varnishes of the heated samples do not undergo any appreciable change in their softening and melting points, thus showing the permanent action of heat with regard to these properties.

222. On the action of heat on the loss in weight and solubility of shellac and temperature coefficient of fluidity.

M. VENUGOPALAN, Ranchi.

A study of the action of heat on the loss in weight and solubility of shellac has been made with a view to finding if any relationship exists between them.

The rate of change of fluidity of shellac with temperature has also been determined under two different conditions to see if it shows any peculiar behaviour with regard to this property.

223. A note on the water absorption of different stick lacs.

M. VENUGOPALAN and S. RANGANATHAN, Ranchi.

With a view to find the resistance to the action of water exhibited by different stick lacs their water absorbing capacities are determined, and also the changes in some of their properties resulting therefrom are noted.



Among the lacs studied Kusum (*Schleichera trijuga*) and Ber (*Zizyphus jujuba*) lacs are able to resist the action of water better than others, both in regard to their property of adhesion and film structure.

Temperature and weight of the films have got remarkable influence on the rate of water absorption and hence the necessity of controlling these factors is indicated.

Further work on the effect of water on some of the mechanical properties of these lacs is in progress.

#### 224. Efficiency of sodium sulphate in comparison with that of khari salt curing and preserving raw hides.

B. M. DAS, B. B. DHAVLE, and B. N. PAL, Calcutta.

Khari salt, which is a natural saline product, consisting mainly of sodium sulphate mixed with a little sodium chloride and good deal of earth and sand, is used in Bengal and Assam for curing raw hides and skins to preserve them for export. The associated earthy matter unnecessarily loads the hides and gives dealers opportunities of increasing the weight of hides by intentional addition of earth and sand to the curing salt. The opportunities of hide adulteration are largely availed of and the malpractice of hide adulteration has brought the Indian dry salted hides into disrepute in the world's markets. A cleaner substitute of the khari salt is a crying need of the Indian hide trade. With the object of finding such a substitute the preservative properties of Glauber salt have been studied in comparison with those of the khari salt. The investigation is not yet complete, but results so far obtained maintain the superiority of the khari over Glauber salt as a hide preservative.

#### 225. Sulphonation of a few oils and the use of the sulphonated products for making fat-liquors.

B. M. DAS, B. B. DHAVLE, and B. N. PAL, Calcutta.

Three oils, linseed, cotton-seed and neatsfoot were sulphonated with 25% of their weight of sulphuric acid (sp. gr. 1.84) in the usual way, care being taken to keep the temperature below 30°. Four mixtures detailed in the paper were made from each of these three sulphonated oils and their suitability with regard to their being used as ready-made fat-liquors for fat-liquoring box sides have been studied. It was found that the mixture of sulphonated neatsfoot oil and neutral castor oil in the proportions of 2 : 1 was the most satisfactory. The mixtures No. I and IV made from sulphonated linseed oil were the next best.

#### 226. Meconic acid of Indian opium.

B. B. DEY, Madras.

The meconic acid prepared in the usual way from the crude calcium salt kindly supplied by Mr. J. N. Rakshit of the Opium Factory, Ghazipur, is found, even after six crystallisations from excess of boiling water containing HCl, to contain another acid of higher carbon content which, from general consideration, appears to be the next higher homologue of meconic acid. The product behaved in all respects like the pure meconic acid obtained from Merck, contained water of crystallisation which was lost completely only on drying at 110° under a pressure of 5 mm. for half an hour, darkened from 260° onwards and charred and decomposed at 280°, etc., but while the commercial meconic acid gave the correct values for carbon and hydrogen, and for water of crystallisation calculated on the basis of the accepted molecular formula  $C_7H_4O_7 \cdot 3H_2O$ , the combustion analyses of the prepared meconic acid as well as of its triethyl ether ester carried out here as well as in a German analytical firm, always



gave such higher values for carbon, varying from 1 to 2 per cent. in excess of that required according to theory, as could hardly be due to experimental error. Attempts to separate the new acid by fractional crystallisation from other solvents have not been successful.

The acid potassium salt of meconic acid does not appear to have been described. This salt is very sparingly soluble, and separates even from moderately dilute solutions; it has the additional advantage of not containing any water of crystallisation. Several estimations of pure meconic acid in solutions of known concentrations, by precipitating the acid potassium salt, and either collecting and weighing this, or titrating it with standard alkali to phenolphthalein, yielded results which were about 3 per cent. too low, but in which the error could be eliminated almost completely by taking the volume of the liquid into consideration and applying a factor.

### 227. Studies in the chemistry of narcotine and its decomposition products.

B. B. DEY, Madras.

The current methods for decomposing narcotine into hydrocotarnine or cotarnine have been re-examined. The action of nitrous acid at  $0^{\circ}$  is found to give rise to a small amount of a nitrogenous product insoluble in cold acids which crystallises from alcohol in colourless prisms melting at  $186^{\circ}$ , the alkaloid being partly recovered unchanged. The reaction is being investigated more closely.

### 228. Hedyotin—the alkaloid of *Hedyotis auricularia*.

S. LAKSMINARAYANAN, Madras.

Several closely agreeing analyses of the purified hydrochloride seem to indicate that its formula was  $C_{16}H_{22}O_3N_2Cl$ . Two concordant analyses of the aurichloride show that it combines with gold chloride in molecular proportions. Carefully conducted Zeisel's experiments revealed the absence of any methoxy group. Several new salts and derivatives of the alkaloid have been prepared and examined.

### 229. Peroxidases.

B. B. DEY, Madras.

The estimation of peroxidase in plant saps is generally carried out by Willstätter's method of oxidising pyrogallol in the presence of hydrogen peroxide into the amorphous purpurogallein. In the course of an examination of the peroxidases of certain plants, particularly, the common Indian vegetables—*luffa acutangula*, *raphanus sativus*, and *daucus carota*, it was observed that the oxidation of hydroquinone to quinone under the same conditions as those specified by Willstätter, took place with greater readiness, the dark shining crystals of quinone beginning to separate out of the clear liquid within five minutes of the addition of the plant extract. The collection and weighing of the crystals is easy to carry out, and the reaction serves admirably for a simple lecture demonstration of the occurrence of peroxidases in plants.

### 230. The colouring matter of some varieties of Hibiscus: preliminary examination.

T. R. SESHADRI, Madras.

Aqueous and alcoholic hydrochloric acid extracts of the petals of the scarlet crimson *H. Rosa Sinensis* and the purple *H. syriacus* have been examined for the following properties: ( ) their absorption spectra, (2)



their colour reaction towards sodium acetate, sodium bicarbonate, and sodium hydroxide, and (3) their dyeing properties towards wool and cotton.

The two varieties are found to contain exclusively anthocyanins which are either identical or are very closely related to one another, and which belong most probably to the cyanidin group.

231. Reactivity of the double bond in coumarins and related  $\alpha\beta$ -unsaturated carbonyl compounds. —Part II.

T. R. SESHADRI, Madras.

The theoretical significance of the series ethyl cinnamate, phenyl cinnamate, coumarin, and benzylidene acetone, is discussed. The reactivity of these compounds has been ascertained by using sodium bisulphite as the addendum in boiling aqueous solution, and they are shown to fall in the order given above of increasing reactivity.

232. Geometrical inversion in the coumaric acid series.

R. RAMACHANDRA RAO, Madras.

The difference in behaviour of the oxyquinoline-acrylic acids, and of their esters on the application of heat (Dey and Seshadri, J.I.C.S., 1927, p. 189), is now shown to be general in the coumaric acid series. The methyl and ethyl esters of coumaric acids, on distillation, pass over readily into the coumarins, whereas with the free acids themselves, the formation of styrenes with the elimination of carbon dioxide, seems to be the sole reaction. Inversion by sunlight is found to proceed with almost equal facility in both cases. A plausible explanation of this observation is given, and the wider phenomenon of geometrical inversion in general is discussed.

233. Coumarin-3-acetic Acids.

A. LAKSMINARAYANA and Y. SANKARANARAYANA, Madras.

These do not appear to have been described in literature. They have now been synthesised from (a) formyl succinic ester, and (b) aceto-succinic ester, by condensation with phenols, the reaction proceeding smoothly in the presence of cold sulphuric acid. The yields are very satisfactory, particularly with the naphthols and meta-substituted phenols; thus from 2 grams of resorcinol 3.5 grams of crystallised 4-methyl-7-hydroxy-3-acetic ester (m.p. 163°) was obtained, which corresponds to a yield of 65% of the pure recrystallised product. The free acids are remarkably stable, in contrast with the coumarin-4-acetic acids which readily decompose at their melting points, or partially even during recrystallisation from a boiling solvent like acetic acid. The reactivity of the methylene group in these acids is being investigated.

234. Action of water on sulphur chloride.

B. SANJIVA RAO, Bangalore.

The reaction between water and sulphur chloride (which is normally very complicated) has been studied by using very dilute benzene solutions of the chloride and analysing the products formed, by the micro-methods described in a previous paper by B. S. Rao and M. R. A. Rao.

The first step in the hydrolysis is an additive product between the two reacting substances :—



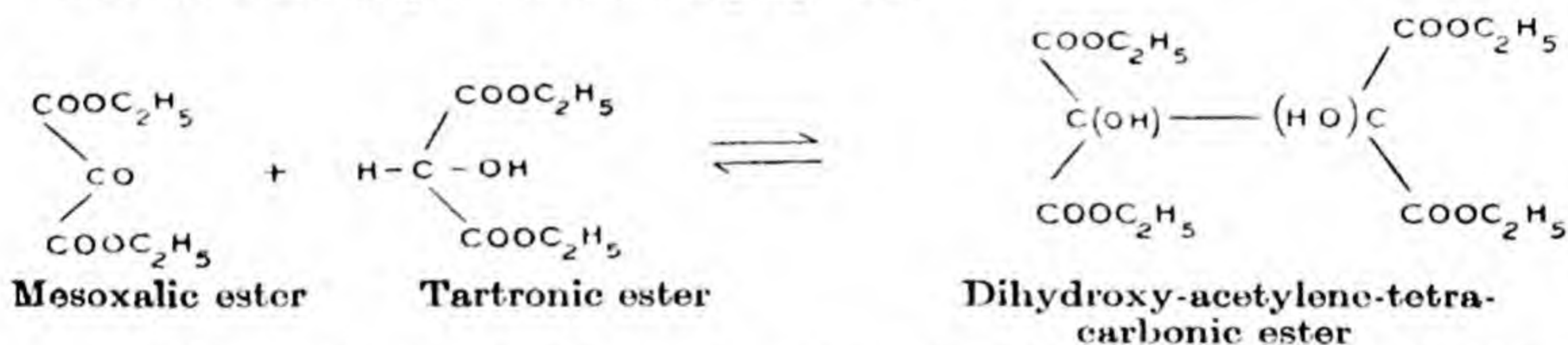


Primary decomposition of this complex yields HCl and (1) H<sub>2</sub>S and SO<sub>2</sub> and (2) sulphur and sulphoxylic acid. (Cf. Noack, Z. anorg. Chem. 1925, 239-262, 146.)

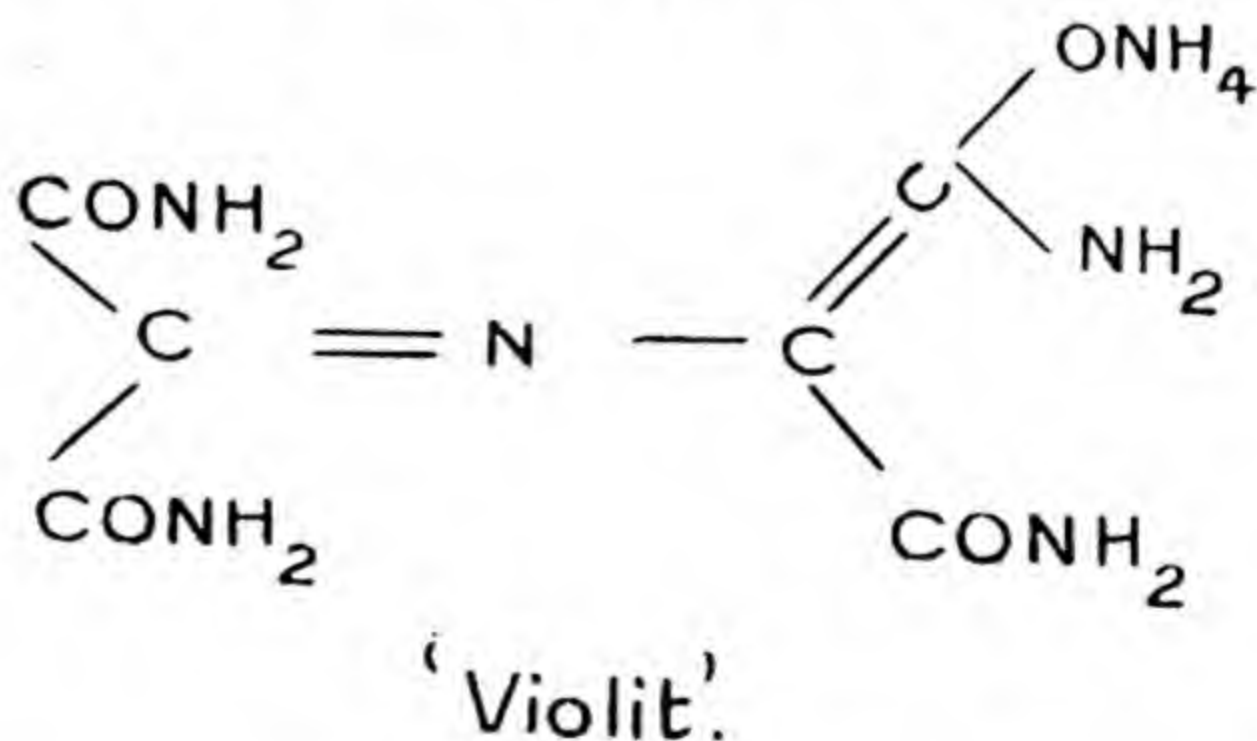
### 235. The murexid reaction with open-chain compounds.

D. D. KARVE, Poona.

The reaction between ammonia and alloxantin, which results in the formation of murexid, is well-known. A similar reaction has now been observed in the case of mesoxalic ester. This latter compound, when mixed with its reduction product tartronic ester, forms an equilibrium mixture according to the following equation:—



This equilibrium mixture when treated with an aqueous solution of ammonia, gives at first a deeply coloured solution, which, when concentrated and finally dried in vacuum over KOH, yields an extremely hygroscopic deep violet powder for which the name 'violit' is proposed. The analysis of this latter agrees with the formula:—



### 236. Condensation of fluorenone and benzophenone with aromatic mono-hydroxy compounds.

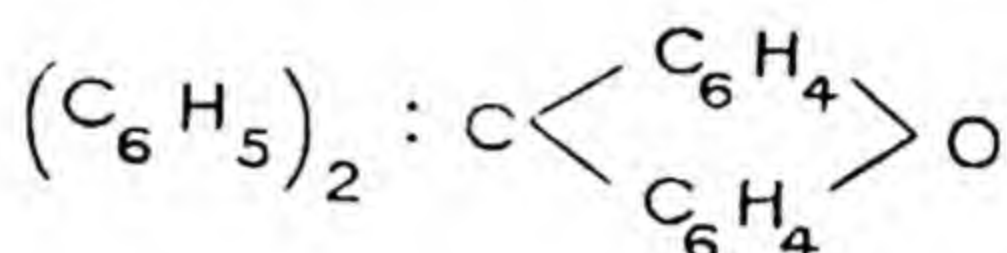
R. N. SEN and S. C. SEN GUPTA, Calcutta.

Condensation of ketones with phenol and  $\alpha$ -naphthol had been carried out previously in presence of benzoic chloride, phosphoryl chloride,

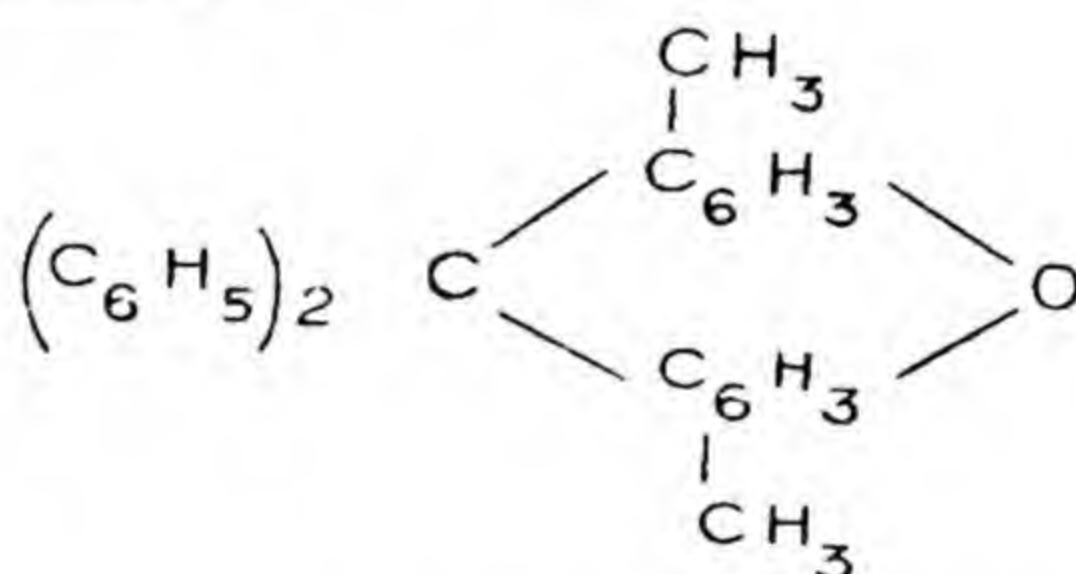


and also acetic acid with hydrochloric acid gas (Dianin, Abs. 1899, 1187; Sen Gupta, Trans. 1914, 399). In this work condensation of benzophenone and fluorenone with monohydroxy phenols has been carried out by heating the ketone and the phenol with fused zinc chloride in an atmosphere of hydrochloric acid gas at  $180^{\circ}$ – $190^{\circ}$ . The condensation takes place both in the ortho and para positions to the phenolic group, giving two products, one insoluble and the other soluble in caustic alkali. Only in the case of ortho condensation 2 molecules of the phenol react, with the pyrone ring formation, tetraphenyl methane derivatives being obtained; in the case of the para condensation reaction takes place with one molecule of the phenol triphenylmethane derivatives being formed. When the para-position to the hydroxyl group is occupied only ortho condensation takes place.

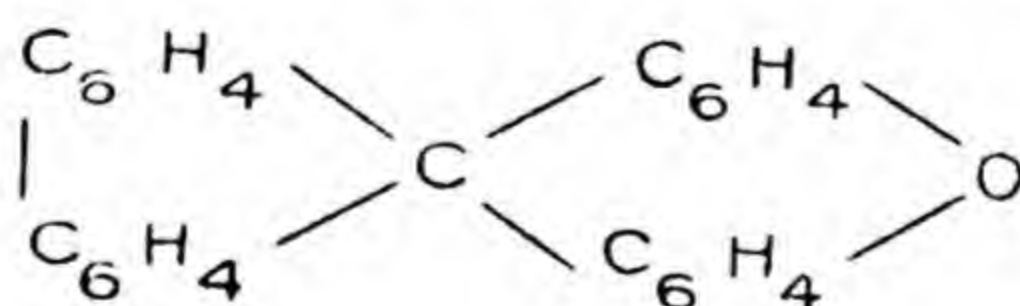
Thus benzophenone and phenol give (1) p-hydroxy triphenyl-carbinol and (2) the anhydride of diphenyl-2 : 2'-dihydroxydiphenylmethane



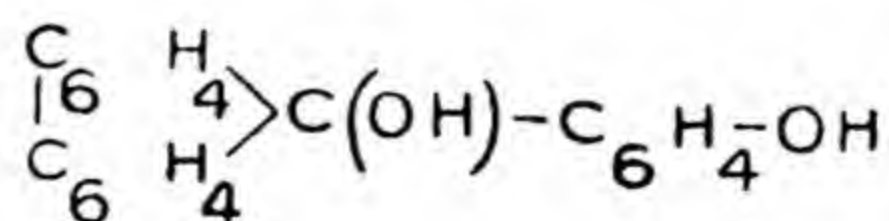
while with p-cresol only one product, namely, anhydride of diphenyl 2 : 2' dihydroxyditolylmethane



is obtained. Similarly with fluorenone two products with phenol are obtained, namely, anhydride of diphenylene 2 : 2'-dihydroxydiphenyl methane

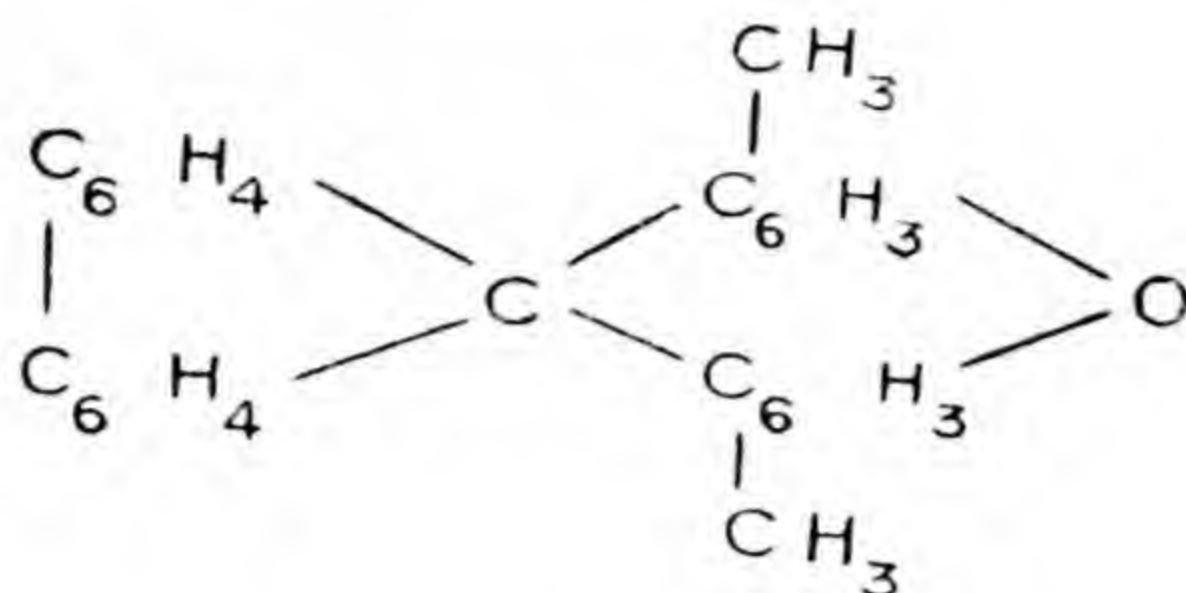


and diphenylene-p-hydroxyphenylcarbinol.



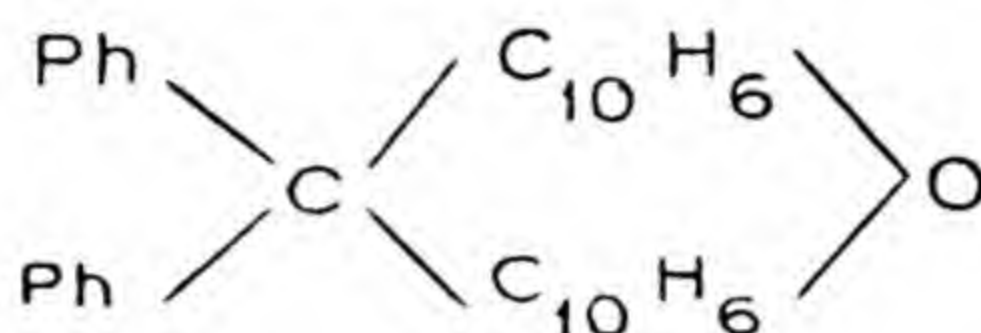
while with p-cresol only one product, namely, anhydride of diphenylene 2 : 2'-dihydroxyditolylmethane



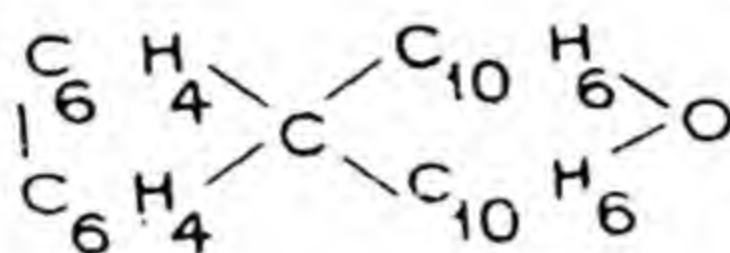


is obtained.

Benzophenone and fluorenone with  $\alpha$ -naphthol give mainly the anhydride of diphenyl 1 : 1-dinaphthylmethane



and anhydride of diphenylene 1 : 1-dihydroxydinaphthylmethane



only a small amount of the alkali soluble product being obtained.

### 237. New cyclohexanone derivatives.

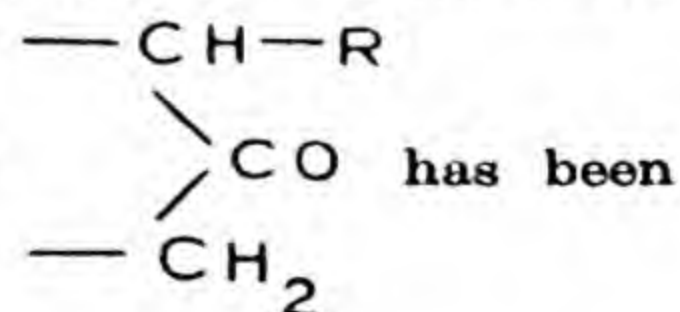
R. N. SEN and J. SARDAR, Calcutta.

Attempts have been made to synthesise ketenes from cyclic ketones, the carbon atom linked to the carbonyl group forming part of a ring. The formation of cyclohexylene ketene from cyclohexanone may be re-

presented thus. Cyclohexanone  $\xrightarrow{\text{KCN}}$  Bisulphite compound  $\xrightarrow{\text{hydrolysis}}$  Nitrile  $\xrightarrow{\text{zinc dust in ethereal solution}}$  1-Hydroxycyclohexane-1-carboxylic acid  $\xrightarrow{\text{PCl}_5}$  Chloro acid chloride  $\xrightarrow{\text{ethereal solution}}$  Cyclohexylene ketene, a yellow liquid boiling

at 84-85° at 16 mm., which gives cyclohexane carboxylic acid (m.p. 28.5°) on heating with water. This scheme of synthesising ketenes from other cyclic ketones such as menthone, carvone and camphor fails as they do not form bisulphite compounds. (Generally hindrance to the bisul-

phite compound formation in such ketones as



noticed.)

$\alpha$ -Bromo-cyclohexanone (Annalen, 358, 195) has been utilised in the preparation of the following interesting cyclohexanone derivatives. By

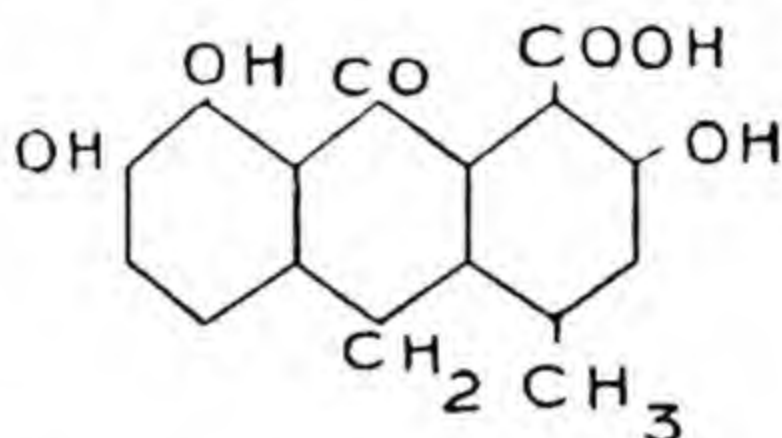


the action of metallic sodium (a) bromocyclohexanone and bromobenzene give 2-phenyl-cyclohexanone boiling at 140–145° at 12 mm. in good yield: (semicarbazone m.p. 192°); (b) bromocyclohexanone itself produces cyclohexanonyl-cyclohexanone, a yellow liquid boiling at 154–158° at 10 mm. (di-semicarbazone m.p. 230°). 2-cyanocyclo-hexanone (Annalen, 441, 68), now prepared in good yield from bromo-cyclohexanone, yields with resorcinol by Hoesch's reaction dihydroxyphenyl-cyclohexanonyl ketone melting at 144°, which gives a di-semicarbazone melting at 244–246°.

### 238. On cochinellic acid.

P. K. PAUL, Calcutta.

Cochinellic acid is the only isolable oxidation product of coccinine which is a trihydroxydimethylanthrone monocarboxylic acid. During oxidation the polyhydric phenol residue of coccinine is destroyed and so from analogy it was expected that an anthrone carboxylic acid of the following constitution would give on oxidation cochinellic acid. The oxidation experiments are in progress.



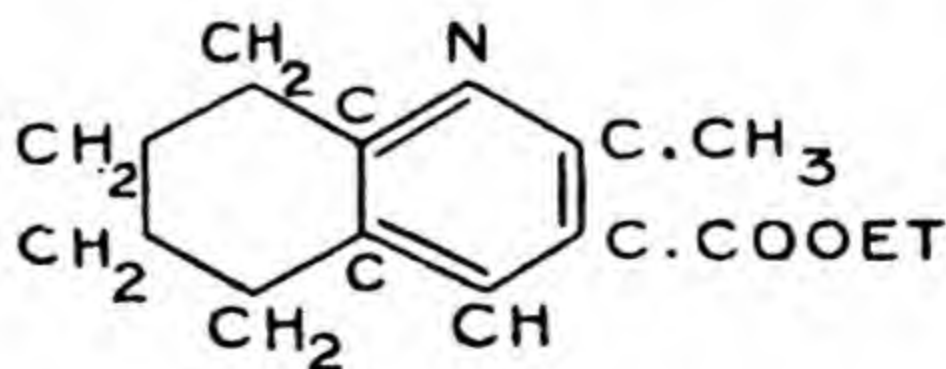
Meconine on condensation with methoxy-*m*-cresotinic acid ethyl ester in presence of aluminium chloride (J. Amer. Chem. Soc., 1927, p. 563), gave a partially demethylated benzyl benzoic acid derivative m.p., 207°, which on ring closure with sulphuric acid gave the corresponding anthrone mono-carboxylic acid m.p. 225°. It was then fully demethylated with acetic acid saturated with HBr m.p. 255°. (decom).

With the same end in view opianic acid was condensed with ethyl meta-cresotinate in presence of 85% sulphuric acid, the condensation product melts at 92°. It was then hydrolysed with 10% alcoholic potash m.p. 255°, which was then reduced with zinc dust and caustic soda and the benzyl benzoic acid derivative melting at 183°, is obtained.

### 239. Synthesis of bz-tetrahydroquinoline derivatives.

UMAPRASANNA BASU, Calcutta.

The reaction between hydroxymethylene-*cyclo*-hexanone and  $\beta$ -amino-crotonic ester is expected to give rise to a bz-tetrahydroquinoline derivative:—



An equimolecular mixture of the two reactants, on several hours' heating yielded mainly a highly refractive liquid, b.p. 160–65°/7 mm., which, on hydrolysis with 10% aqueous potash gave an acid, m.p. 224–25°

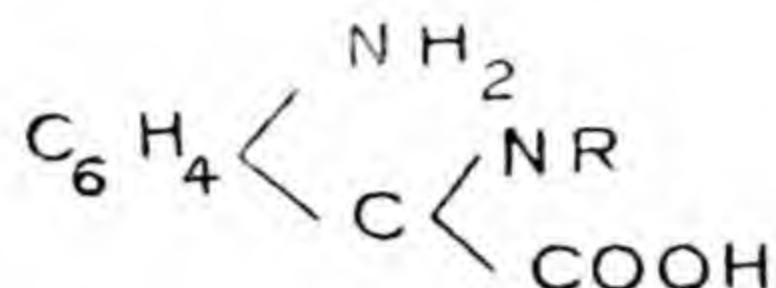


(decomp). A crystalline solid having the same percentage composition was also isolated from the reaction mixture. The constitutions of the two condensation products and the mechanism of the reaction are under examination.

240. Attempts to prepare 3:4-benzo-iso-quinoline.

K. S. NARANG and J. N. RAY, Lahore.

Isatinic acid in alkaline solution gives with aromatic amines acids of the type

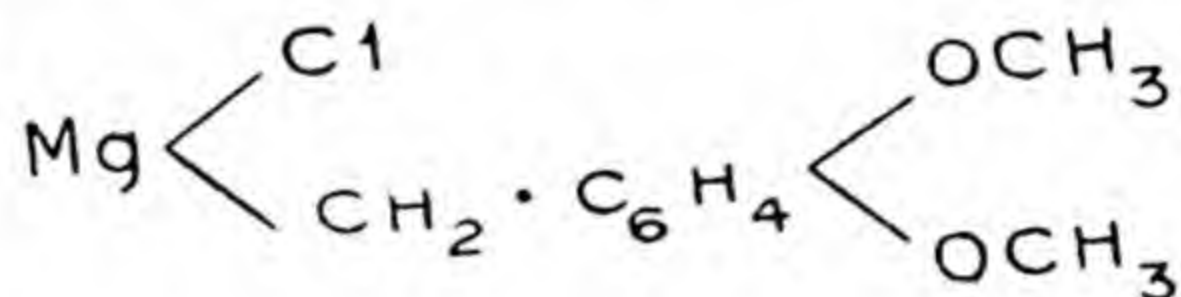


Attempted Pschorr synthesis on these compounds are described.

241. Experiments in the synthesis of brazilin (V).

M. ABDUL HAQ, J. N. RAY and R. ROBINSON, Lahore.

M-methoxy phenoxy acetyl chloride with

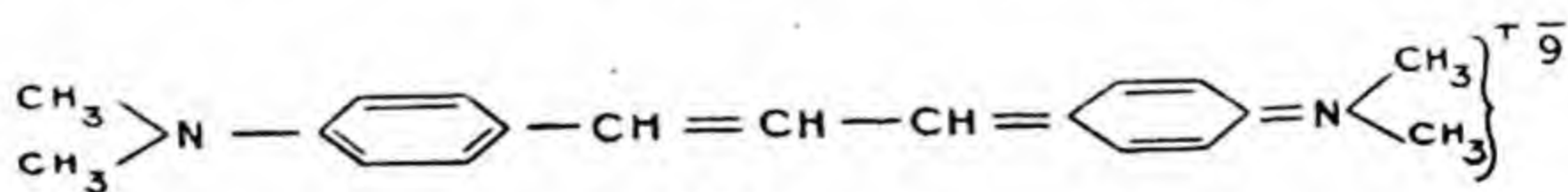


give a ketone which forms a cyanhydrin. Attempts are recorded of its transposition to trimethyl brazilin.

242. Photosensitising dyes.—Part I. The preparation of a new carbocyanine.

M. Q. DOJA, Patna.

(A) Several plausible methods for the preparation of a new carbocyanine



(A)

have been elaborated and their relative merits discussed. The various stages in the proposed synthesis which have been achieved so far are given.

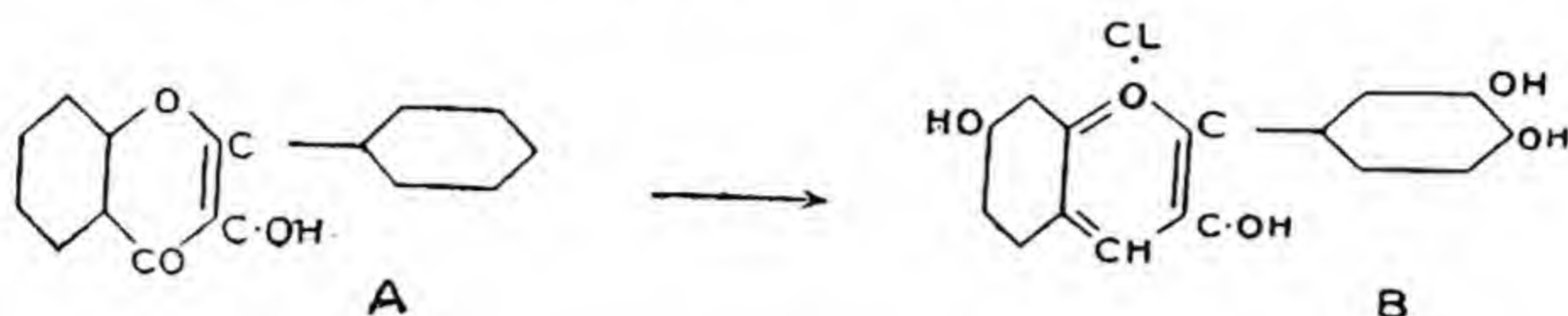
243. The rise and fall of a biochemical hypothesis.

M. NIERENSTEIN, Bristol, England.

Cyanidin, the colouring matter of corn flower, has been shown by Willstätter to give a beautifully crystallising chloride,  $\text{C}_{15}\text{H}_{11}\text{O}_6\text{Cl}$  and to yield phloroglucinol and protocatechuic acid on hydrolysis. Since

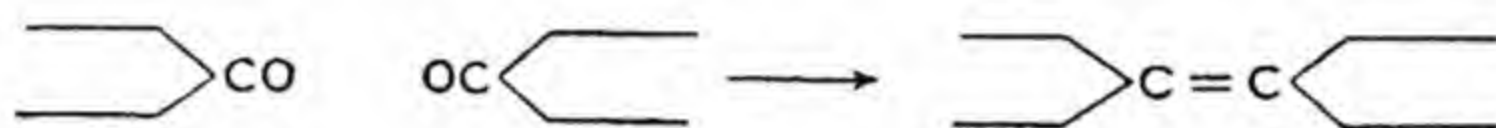


quercetin is supposed to yield cyanidin chloride on reduction in hydrochloric acid solution, formula B is assigned to it.

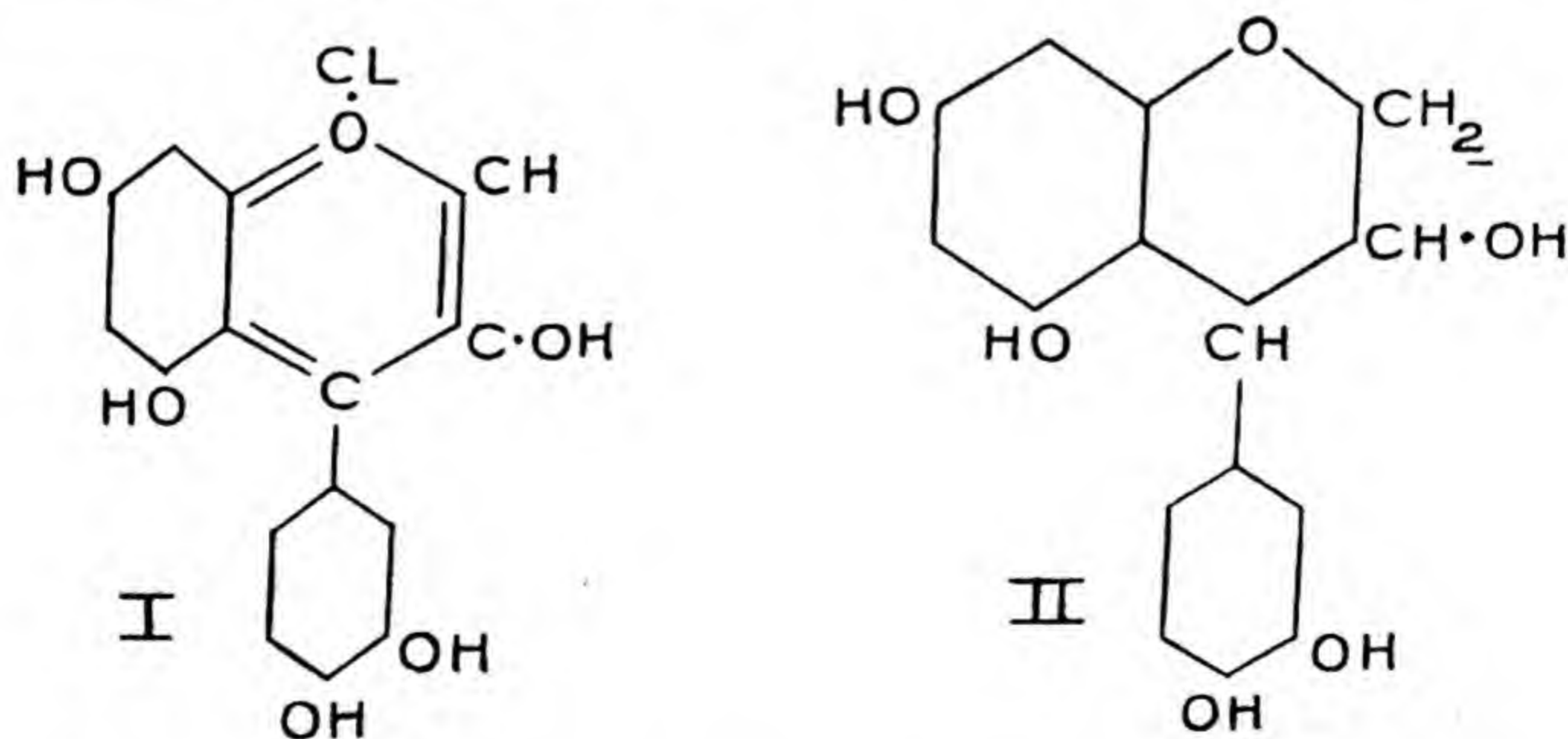


The botanical evidence was, however, contrary to the chemical interpretation put forward by the supporters of the reduction theory which has been upheld by Willstätter and Everest.

Willstätter and Everest synthesised cyanidin from quercetin and found it to be identical with natural cyanidin from corn flowers and roses. Malkin and Nierenstein showed that the production of cyanidin chloride from quercetin was quite unexpected since fluorone, xanthone, pyrone, etc., lead to dimolecular products on reduction in acid solution. They showed that the reduction proceeds normally as follows;—



It has also been shown that the methods used for the comparison of the synthetic products with natural ones, viz., (1) the colour reactions, (2) the absorption spectra, (3) the general crystallographical appearance, are unreliable. Even the X-ray analysis of cyanidin chloride and the synthetic cyanidin chloride (3, 5, 7, 3', 7', pentahydroxy flavyllium chloride) shows not a single crystal spacing which is common to both the substances. Freudenberg has succeeded in reducing cyanidin chloride to epi-catechin. From a series of investigations published by me there is not the slightest doubt that catechin is represented by formula (II), which would suggest formula (I) for cyanidin chloride.



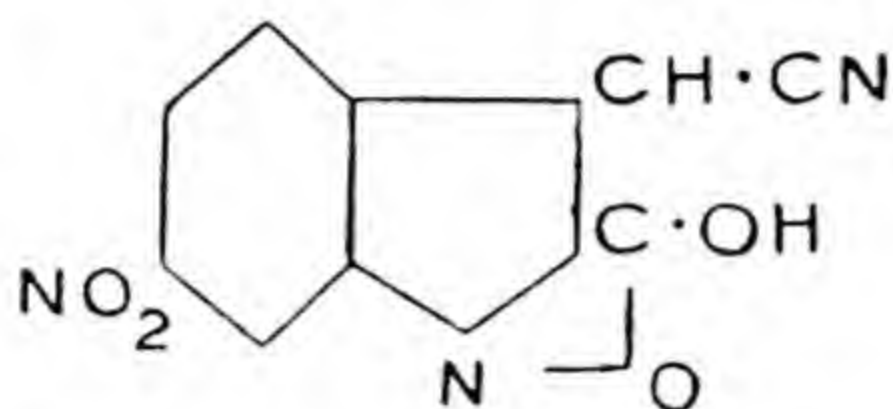
But the constitution is not definitely settled since we have not succeeded in the epimerisation of catechin to Freudenberg's epicatechin and in its production from cyanidin chloride on reduction.



## 244. A new synthesis of indoles.

Y. G. DORAISWAMY, Madras.

In the course of an investigation of the relative activity of the chlorine atom in the chloro-nitro-benzenes, chloro-cyano-benzenes, and chloro-benzoic acids, by condensing them with the sodium derivatives of certain ketones and esters and measuring the amounts of the chlorine-free condensation products, it was observed that the reaction between cyanacetamide and cyanacetic ester, and 1-chloro-2:4-dinitrobenzene led to the formation of a considerable amount of a product which, from analysis and chemical behaviour, appears to have the constitution given below :—



It crystallises from boiling acetic acid in deep orange-red rhombic plates melting at  $184^{\circ}$ . The crystals become deep blue in colour in contact with even a trace of alkali, and dissolve completely on boiling with  $2N\text{—KOH}$  to a dark indigo-coloured solution from which, on cooling, a potassium salt crystallises out in soft needles having a dark green metallic reflex. It is found to be the potassium salt of an acid, which is liberated on the addition of dilute mineral acids as a pale yellow solid, redissolving in cold sodium bicarbonate to the original blue solution.







# INDIAN SCIENCE CONGRESS.

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Nineteenth Annual Meeting,  
BANGALORE, 1932.

ABSTRACTS OF PAPERS.

Section of Chemistry.

*President :—Prof. P. Rây, M.A.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







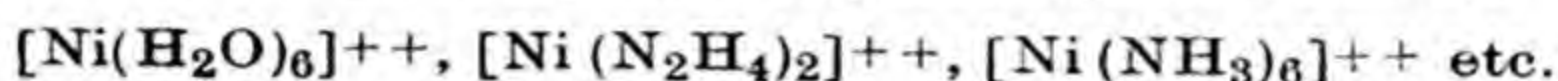
## Section of Chemistry.

### *Abstracts.*

1. Relation between the absorption spectra and the magnetic susceptibilities of paramagnetic solutions.

D. M. BOSE and S. DATTA, Calcutta.

It is shown in a note communicated to the Physical Section of this Congress that associated complexes of paramagnetic ions like



are formed by the interpenetration of the electron charge of the paramagnetic ion with those of the surrounding dipole molecules forming the complex. The magnetic moment of the ion present in the complex can in general be represented by a formula proposed by Van Vleck

$$\mu = \sqrt{4s(s+1) + l(l+1)}$$

where  $s$  = the resultant of the spin moments of the electron,

$l$  = " " orbital moments. The more intimate the interpenetration, the less possible it is for the orbital moment of the paramagnetic ion (represented by the quantum number  $l$ ) to orient itself in the external magnetic field and therefore to contribute its full quota to the magnetic moment of the latter. The measure of the association affinity between the ion and the dipole molecules surrounding it, is the deviation of the magnetic moment of the complex from the value calculated according to the above formula.

On the other hand if  $\nu_g$  is the absorption frequency of the paramagnetic ion in the gaseous state and  $\nu_s$  that of the same ion when forming part of a complex radicle, then it can be shown that  $h\nu_s = h\nu_g + w$ ; where  $w$  is the work done in breaking up the association of the ion with the surrounding dipole molecules. Thus the strength of this association is manifested (i) by the deviation of the magnetic moment of the complex from the theoretical value to be expected for the simple ion and (ii) by the shift of the absorption spectra due to the complex, towards the violet side. It is shown for a number of aqueous solutions containing paramagnetic complex ions that such a correlation actually exists.

2. A new constitutional formula for benzene.

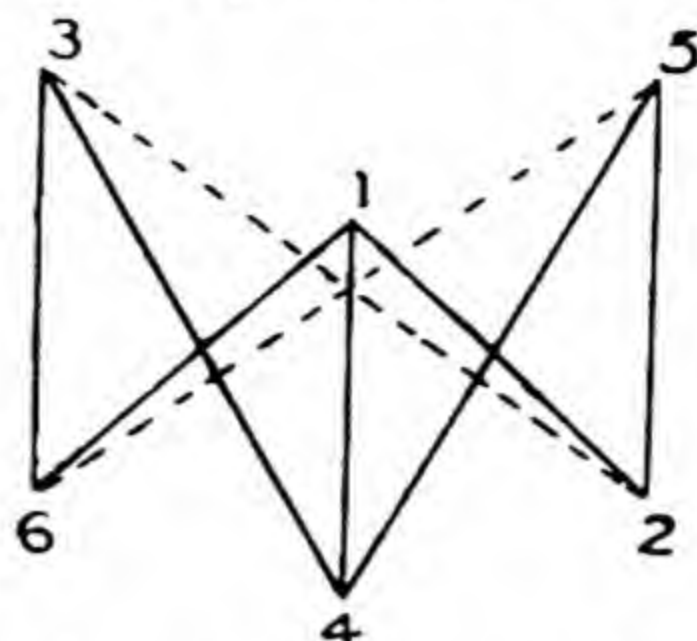
P. GUHA, Bangalore.

The merits and demerits of the various proposed structural formulae for benzene are well known. The following new structure is tentatively put forward as explaining most of its well known chemical properties.

In the new formula, the six carbon atoms are placed at the corners of a regular prism, as in the well known prism formula of Ladenburg, where are to be found six meta and three para linkages. In the proposed formula six ortho and three para linkings are postulated, diagonal corners of the prism faces being ortho and those occupying the ends of the vertical



edges being para. The meta linkings are dispensed with. The new formula, in perspective, may be represented as,



A critical discussion of the chemical and physical properties of benzene with reference to the proposed new formula and the older formulae is made.

### 3. Raman spectra of optical isomers.

GAJANAN V. NEVGI and S. K. KULKARNI JATKAR, Bangalore.

The Raman spectra of the following optical isomers have been studied:—(1) *d.* Pinene, (2) *l.* pinene, (3) *d.* Sabinene, (4) *l.* Sabinene, (5) *d.*  $\Delta_3$  carene, (6) *l.*  $\Delta_3$  carene. A special tube had to be designed to give satisfactory results with 7-8 c.c. of pure substances available. The spectra of *d.* and *l.* Pinene have been fully analysed and have been found to be identical except some variations of the intensities. In both the pinenes a characteristic band of definite structure has been observed which contains a series of 8 sharp lines in agreement with the observations by Bonino and Cella (*Nature* 126, p. 915; 1930). The spectra of the sabinens and also of  $\Delta_3$  carenes are also identical for the *d.* and *l.* forms.

Some of the shifts have been identified with definite chemical linkages.

### 4. Raman effect in some reduced derivatives of benzene.

GAJANAN V. NEVGI, Bangalore.

Raman spectra of the following substances have been studied:—(1) cyclohexane (2) cyclohexene (3) methyl cyclohexane (4) cyclohexyl acetate (5) cyclohexyl propionate (6) cyclohexanol (7) orthomethyl cyclohexanol (8) meta methyl cyclohexanol (9) para methyl cyclohexanol (10) cyclohexanone (11) ortho methyl cyclohexanone (12) para methyl cyclohexanone.

The spectrum of cyclohexanol is not much different from its homologues. The isomers o. m. and p. of methyl cyclohexanols differ in their spectra only in the smaller shifts. The longer shifts are accompanied by changes in intensities and not in value. There are marked differences in the o. and p. methyl cyclohexanones. Some of the shifts have been identified with definite chemical bonds.

### 5. Raman spectra of amyl alcohols.

GAJANAN V. NEVGI and S. K. KULKARNI JATKAR, Bangalore.

The Raman spectra of the isomeric amyl alcohols have been studied using 4046 and 4358 as exciting lines from a 3,000 c.p. Heraus Mercury lamp and the shifts obtained give the following wave lengths in Å. U for the infra-red absorption:—

(1) *N.* butyl carbinol.

3.37, 3.41, 3.48, 6.9, 7.7, 8.98, 9.4, 9.88, 10.43, 11.2, 11.83, 12.98.



## (2) Isobutyl carbinol.

3.38, 3.42, 3.48, 6.87, 7.61, 8.82, 9.41, 10.26, 10.49, 11.1, 12.03, 13.07.

## (3) Sec. butyl carbinol.

3.37, 3.42, 3.48, 6.84, 8.86, 9.48, 9.77, 10.39, 11.0, 11.95, 12.97, 21.9, 26.7.

## (4) Methyl n. propyl carbinol.

3.37, 3.42, 3.48, 6.91, 7.69, 8.91, 9.76, 10.54, 11.25, 12.05, 20.1, 29.9.

## (5) Diethyl carbinol.

3.37, 3.42, 3.48, 6.88, 7.65, 8.88, 9.69, 10.58, 11.93, 13.5, 20.5, 30.9.

## (6) Dimethyl ethyl carbinol.

3.36, 3.42, 3.48, 6.86, 7.76, 8.44, 9.48, 10.74, 11.36, 13.76, 19.0, 28.0, 38.8.

The differences among various isomers are shown in the long wave lengths, i.e., beyond  $13\mu$ . The shift  $770 \Delta\nu$  attributed to the OH group in the amyl alcohols is present in all the primary alcohols but its value in the secondary alcohols is less and still less in tertiary amyl alcohol. The following are the values of the shifts: (1) 770, (2) 765, (3) 771, (4) . . . , (5) 741, (6) 727.

The spectrum of tertiary amyl alcohol is much different from the rest, which is to be expected from its different chemical structure. Some of the shifts have been identified with definite chemical bonds.

## 6. A note on the anomalous X-ray spectra of the simple and the complex iodates of titanium and tin.

P. RÂY, Calcutta.

The simple and the complex iodates of titanium have been found to resemble the corresponding tin compounds in all chemical and physical properties including their molecular volume. The X-ray spectra of potassium stanni-iodate and potassium titani-iodate are perfectly identical, indicating a close isomorphous relationship. Curiously enough, the simple titanium iodate gives the same X-ray spectra as these two complex salts. What is still more strange, a stoichiometrical mixture of potassium iodate and titanium iodate gives an X-ray spectrum, in which all the lines due to titanium iodate vanish and even those of potassium iodate become very faint. No explanation can as yet be suggested for these anomalies.

## 7. Effect of mechanical and chemical colloidalisation on the diamagnetism of antimony.

S. S. BHATNAGAR, R. N. MATHUR, and MULKH RAJ VARMA, Lahore.

The magnetic properties of elements in the colloidal state have seldom been investigated. In the case of antimony, however, it was found by some workers that the diamagnetism of this element decreases considerably on mechanical and chemical colloidalisation. These experiments have been repeated but the results show that the fall in diamagnetism observed by previous workers is mostly due to the oxide formation. Antimony powders and sol contain enough of antimony oxides to be estimated by ordinary methods. Moreover, after washing the powders with suitable reagents to remove the oxides, practically no fall in diamagnetism is observed.

## 8. The dimorphism of trilaurin.

R. K. VALVEKAR and S. K. KULKARNI JATAKAR, Bangalore.

In continuation of the previous work (reported in Allahabad Science Congress, 1930) the cooling curve of specially purified trilaurin revealed the



temperature at which the molten liquid of the stable form changes into unstable form with absorption of heat before solidifying, the phenomenon having escaped the attention of previous observers as it could be ascribed to undercooling.

The heat of this transformation is being determined by the method of twin calorimeters.

9. The 'corona pressure' phenomenon in electric discharges due to alternating fields of low frequency.

S. S. JOSHI, Benares.

It was observed incidentally that when an alternating P.D. of the order of 15,000 volts (r. m. s.) was applied to a gas at a moderate pressure contained in the annular space of two tubes sealed coaxially as in the Siemens' ozoniser, a sudden pressure rise, followed by a slower pressure change, was produced just after the secondary P.D. was switched on. Reverse series of pressure changes is produced soon after the cessation of the current. Results are obtained bearing on the nature of the initial pressure change.

10. Studies on the dependence of optical rotatory power on chemical constitution. Part XIII. Naphthylene derivatives of stereoisomeric iminocamphors and methylenecamphors.

B. K. SINGH and BHUTNATH BHADURI, Cuttack.

Naphthylenediamines (1:2 and 1:5) have been condensed with camphorquinones (*d*, *l*, *dl*) and oxymethylenecamphors (*d*, *l*, *dl*). The rotatory powers of the enantiomers are found to be identical. The rotations of benzocamphanoquinoxalines (*d*, *l*) are so low that the sign of their rotations is reversed. 1:5 Naphthylenebisimino-, and 1:5 naphthylenebis-aminomethylene camphors are found to have much lower rotations than the corresponding 1:4 compounds. The introduction of an amino group in the 5-position of  $\alpha$ -naphthyliminocamphor lowers the rotation and acetylation still further lowers the same. 1:5 Naphthylenebisaminomethylenecamphor obeys the simple dispersion law.

11. Studies on the dependence of optical rotatory power on chemical constitution. Part XIV. Stereoisomeric amidomethylene-, and imido-methylenecamphors and their derivatives.

B. K. SINGH and B. BHADURI, Cuttack.

It is found that the rotatory dispersion of amidomethylene- and imidomethylene-camphors can be expressed by the one-term equation of Drude.

The rotatory dispersion of the *dextro* and *laevo* forms is identical, and this supports Pasteur's law of molecular dissymmetry.

Benzalamidomethylenecamphor has been obtained in three forms *d*, *l*, *dl*. Its specific rotatory power is more than twice as large as that of the amidomethylenecamphor.

The *internally compensated* imidomethylenecamphor was prepared in two ways by the condensation of (1) amidomethylene-*d*-camphor with oxymethylene-*l*-camphor and (2) amidomethylene-*l*-camphor with oxymethylene-*d*-camphor. The products were in both cases inactive and identical as they had the same m.p. and mixed m.p.



12. Studies on the dependence of optical rotatory power on chemical constitution. Part XV. Chloroaryl derivatives of stereoisomeric methylenecamphors.

B. K. SINGH and BHUTNATH BHADURI, Cuttack.

The chloro derivatives (*mono*, *di*, *tri*) of anilinomethylenecamphors (*d*, *l*, *dl*) have been prepared. The rotatory power of the optically active isomerides (*d*, *l*) determined in six solvents and for eight to nine wavelengths ( $\lambda=4800$  to  $6708 \text{ \AA}$ . U) are found to be identical and can be expressed by the one term simple dispersion equation of Drude,

$$[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$$

The polar effect as deduced from the electronic theory is traceable in optical activity; the replacement of a hydrogen atom by a negative group such as Cl, diminishes the rotation of the parent compound; further substitution by a similar group as in dichloro and trichloro derivatives of anilinomethylenecamphor results in progressive diminution of the rotatory power.

13. Studies on the dependence of optical rotatory power on chemical constitution. Part XVI. Bromo- and iodoaryl derivatives of stereoisomeric methylenecamphors.

B. K. SINGH and BHUTNATH BHADURI, Cuttack.

The optically active (*d* and *l*) bromo- and iodoanilino methylenecamphors have identical rotation and are found to obey the simple dispersion law of Drude.

Substituent influence on rotatory power in the optically active compounds is represented by  $H > CH_3 > Cl > Br > I$ ; the series being identical with the polar series; positions of iodine and chlorine being interchanged. The influence of the solvents and position isomerism on rotatory power is discussed.

14. Studies on the dependence of optical rotatory power on chemical constitution. Part XVII. Nitro- and carboxyaryl derivatives of stereoisomeric methylenecamphors.

B. K. SINGH and T. P. BARAT, Cuttack.

The nitro and carboxy derivatives (*o*, *m*, *p*) of anilinomethylenecamphors (*d*, *l*, *dl*) have been prepared. The rotatory powers of the enantiomers are identical and can be expressed by the simple dispersion equation of Drude.

Substituent influence on rotatory power in the optically active compounds is represented by  $NO_2 > H > CH_3 > Cl > Br > I$  for the *ortho* and *para* derivatives;  $COOH$  occupying an intermediate position varying with the nature of the solvent in which the rotatory power is determined. This series is, on the whole, nearly identical with the 'polar' one.

15. The refractive and rotatory dispersion in terpenes. Part I.

R. PADMANABHAN and S. K. KULKARNI JATKAR, Bangalore.

The optical dispersion of *d* and *l*-pinene, *d* and *l* sabinene and *d* and *l*  $\Delta_3$  carene, isolated in our laboratory from various essential oils and



purified by repeated distillation and crystallisation, has been studied in the visible and glass ultraviolet using the lines from the mercury arc, iron arc and a hot cathode helium arc, and was found to be normal. The rotatory dispersion was measured with a modified form of the three field polarimeter in conjunction with a constant deviation spectroscope and the refractive indices with the Pulfrich Refractometer.

Apparatus is being constructed to extend similar measurements in the ultraviolet where the above substances show absorption.

#### 16. Influence of geometrical isomerism on optical rotation.

P. NEOGI and A. K. SEN.

Salts of acids, which are geometrical isomers, with quinine, quinidine, cinchonine, cinchonidine, strychnine, morphine and brucine have been prepared and their optical rotation compared.

#### 17. Dissociation pressures of cadmium carbonate.

P. Y. NARAYAN, Bangalore.

The pressures of carbon dioxide in equilibrium with cadmium carbonate and cadmium oxide developed as a result of the dissociation of the former are measured at different temperatures by the static method.

The results obtained agree very satisfactorily with the values calculated from the well known Nernst's approximation formula,

$$\log p = \frac{-Q}{4.571 T} + 1.75 \log T + 3.2,$$

using Thomsen's value for the heat of dissociation. The results, however, differ from the values obtained by Centnerszwer and Andrussov (*Zeit. Physikal Chemie, III*, 79, 1924) at low pressures.

#### 18. The density and compressibility of sulphur hexafluoride.

G. GUNDU RAO, K. L. RAMASWAMI, and H. E. WATSON, Bangalore.

Sulphur hexafluoride has been prepared by the direct combination of sulphur with fluorine generated by the electrolysis of fused potassium bifluoride. The gas after long standing over strong alkali and drying, was purified by repeated fractional distillation at low temperatures.

The experiments were done in the same apparatus previously described (*Ind. Sc. Congress*, Sec. III, Abs. 215). The values of the compressibility coefficient  $A$  at  $+25^\circ$  and  $-80^\circ$  are respectively  $0.012 \pm 0.001$  and  $0.045 \pm 0.001$ .

Work on the limiting density is proceeding with a view to redetermine the atomic weight of fluorine.

#### 19. Variation of surface tension and viscosity of different solutions with dilution.

D. N. CHAKRAVARTI and U. D. MUKERJI, Amraoti.

The surface tension and viscosity of the following sols were determined at different dilutions:—

- (1) Ferric phosphate, (2) Ferric arsenate, (3) Ferric tungstate, (4) Ferric hydroxide, (5) Chromium arsenate, (6) Chromium hydroxide, (7) Arsenic sulphide, (8) Ceric hydroxide, (9) Aluminium hydroxide, (10) Zirconium borate, (11) Molybdic acid, (12) Antimonic acid.



It was found that the surface tension of the colloids increases with the decrease in the concentration whereas the viscosity decreases with the decrease of concentration. The change of surface tension with concentration can be expressed by the following empirical formula :—

$$S = S_0 e^{A - BC^2},$$

where  $S$  = Surface tension of colloids,  $S_0$  = Surface tension of the medium,  $A$  and  $B$  are constants depending on the nature of the colloid,  $C$  = Concentration expressed in number of grams per litre.

In the case of viscosity also a similar formula, namely

$$\eta = \eta_0 e^{A_1 + B_1 C^2}$$

holds good.

We have verified these equations with above solutions by plotting  $\log S$  and  $\log \eta$  against  $C^2$  and in every case we get straight lines.

## 20. Solubility of silver chloride in water, nitric acid and dilute aqueous solutions of alkali nitrates.

P. C. DAVE and K. R. KRISHNASWAMI, Bangalore.

The solubility of coagulated silver chloride in  $H_2O$ , and in dilute aqueous solutions of  $HNO_3$ ,  $KNO_3$ ,  $NaNO_3$  and  $NH_4NO_3$  was determined in different concentrations of the solvent in the temperature-range 0–50, employing the nephelometric method. The results obtained are discussed in the paper.

## 21. Effect of polar and non-polar solvents and their mixtures on the solubilities of benzoic and salicylic acids.

P. G. DESAI, Bombay.

The solubilities of benzoic and salicylic acids have been determined in benzene, toluene, hexane, xylene, carbon-tetrachloride, chlorobenzene, nitrobenzene, chloroform, aniline, acetone, and methyl, ethyl, (normal) propyl and (normal) butyl alcohols and varying percentages of their mixtures.

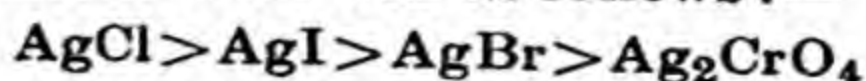
It is found that in presence of varying percentages of the solvents, in certain mixtures, maxima are obtained when solubilities are plotted against percentage amounts of the solvents. Compound formation was also noticed in certain cases.

Work on the changes of the dipole moments of the mixtures of the solvents in presence of the solute is in progress.

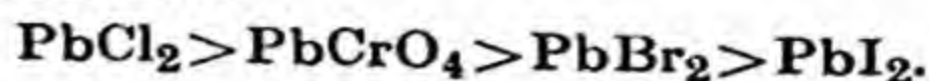
## 22. Action of glycine and alanine on the insoluble salts of silver and lead.

H. M. MAPARA and A. M. PATEL, Bombay.

It was observed that, if to a solution of silver nitrate or lead nitrate there was added a solution of potassium chloride or bromide or iodide or chromate in quantity sufficient to produce precipitation, no precipitate was formed if there had been previously added to either reactant a definite amount of glycine or alanine. It was found that with the increase in the concentrations of the salt solutions of silver or lead, the amounts of glycine or alanine required also increased. The order of the amounts of glycine or alanine in the case of silver salts was as follows :—



while in the case of lead salts





It was also found that the addition of increasing amounts of the chloride, bromide, iodide or chromate of potassium to a definite amount of either  $\text{AgNO}_3$  or  $\text{Pb}(\text{NO}_3)_2$  did not affect the amounts of glycine or alanine required.

The clear solutions obtained were not colloidal. It is believed that chemical complexes are formed in solution. Further work on the elucidation of these is in progress.

### 23. On Langmuir's theory of adsorption.

A. GANGULI, Chandernagore.

Previously Langmuir's formula for adsorption and the value of Langmuir's constant were divided statistically (K. C. Kar and A. Ganguli, *Phys. z.* 30, 918 (1929), Ganguli, *J. Phys. Chem.*, 34, 665 (1930)) and it was found that although the  $k_{\text{cal.}}$  agreed with  $K_{\text{obs.}}$  computed from results of Standard authors for ordinary temperature, discrepancies arose in some cases when the temperature was very low. In the present paper, the methods are modified by taking into consideration that the adsorbed molecule may occupy 'n' adsorption centres and Freundlich's adsorption isotherm is deduced as a first approximation. The Langmuir's constant

$$k = \left\{ \frac{(2\pi mkT)^{\frac{1}{2}}}{\zeta} e^{-\frac{\alpha}{kT}} \right\}^{\frac{1}{n}}$$

where  $\zeta = nh$  and  $\alpha$  is adsorption potential. Again by following Stern's method it is found that the number of adsorbed molecules

$$N_a = \frac{N_o}{nN} \frac{\left\{ \frac{p}{(2\pi mkT)^{\frac{3}{2}}} \cdot \frac{h^3}{kT} e^{\frac{\chi}{kT}} \right\}^{\frac{1}{n}}}{1 + \left\{ \frac{p}{(2\pi mkT)^{\frac{3}{2}}} \cdot \frac{h^3}{kT} e^{\frac{\chi}{kT}} \right\}^{\frac{1}{n}}}$$

where  $N_o$  is the total number of adsorption centres, and 'n' is the number of the centres occupied by an adsorbed molecule and  $\chi$  is identified with  $\alpha$ . Consequently the expression for ionic adsorption (Kar and Ganguli, *Z. f. Phys.*, 61, 411, 1930) is modified and we obtain for monovalent ions

$$a = \alpha c^{\frac{1}{n}} \left( e^{\frac{EF}{RT}} - e^{-\frac{EF}{RT}} \right)$$

where the constant  $\alpha$  is the reciprocal of the Langmuir's constant 'k'.

### 24. Theories of periodic precipitation.

A. C. CHATTERJI.

Recently attempts have been made to revive the Ostwald's Supersaturation theory of periodic precipitation. As emphasised in previous papers, the one necessary condition of this theory is that the sparingly soluble salts should be capable of forming supersaturated solutions easily.

In this paper, the quantity of the various salts that can remain suspended in a gel has been determined. A few of the results obtained are given below.



No.	Salt.	Medium.	Suspended amount.	Ratio (Quantity suspended : solubility in water).
1.	Silver chromate	.. 2.3% gelatine	$4.6 \times 10^{-3}$ N	26.6
2.	Silver chloride	.. 3.0% gelatine	$7.61 \times 10^{-3}$ N	539.0
3.	Lead chromate	.. 3.0% gelatine	$2.93 \times 10^{-2}$ N	$3.95 \times 10^5$
4.	Lead chromate	.. 1.7% Agar	$7.6 \times 10^{-3}$ N	$1.02 \times 10^5$
5.	Mn. sulphide	.. 2.0% Agar	$3.432 \times 10^{-2}$ N	$3.432 \times 10^5$
6.	Silver sulphide	.. 3.0% gelatine	$4.44 \times 10^{-3}$ N	$1.037 \times 10^{14}$

From the above table it is apparent that very large quantities of these sparingly soluble salts can remain suspended in the gel when compared to their normal solubilities.

In a series of preliminary experiments conducted in this laboratory by M. R. Nayar, it was not possible to produce supersaturation with ammonium oxalate, potassium nitrate and sodium nitrate beyond 1.25 times their normal solubility. Similar results are obtained by Tammann (*Zeit Anorg. Chem.*, 1931, 200, 57) with nickel sulphate, potassium iodide, etc.

Moreover it has been our experience that it is difficult to produce supersaturation with salts that do not show a rapid increase in solubility with rise of temperature. Hence it is rather difficult to accept the view that such large quantities of so sparingly soluble salts can remain in supersaturated condition when more easily soluble salts cannot be made to go into supersaturation beyond 1.5 times the normal solubility.

The influence of gels on the solubility of salts is under examination.

## 25. Studies in the viscosity variations due to chemical reactions in liquid medii.

S. S. JOSHI and SUSARALA RAJU, Benares.

This has been investigated in the hydrolysis of methyl acetate, ethyl acetate, sucrose, maltose, lactose, acetic anhydride, and during the mutarotation of glucose and fructose under a wide range of conditions as to temperature and concentration. The results obtained show that the viscosity change can be utilised with much convenience and considerable precision to follow the progress of specially monomolecular reactions produced in liquid medii. Thus for instance in the hydrolysis of methyl acetate in the presence of 0.333 N and 1.6 N HCl values for the velocity coefficient calculated from the observed viscosity variation were  $2.44 \times 10^{-3}$  and  $13.2 \times 10^{-3}$  respectively. These compare well with the results of Lewis and Lamble (*J.C.S.*, 1914, 45, 2330), who found the above constant under above conditions to be  $2.33 \times 10^{-3}$  and  $13.68 \times 10^{-3}$  respectively. A similar agreement is obtained for the values of the temperature coefficient of the velocity constant for the above change when determined by the present and the usual chemical method. An interesting case was observed in the hydrolysis of the bioses and in the mutarotation of the monoses mentioned above. This did not show any sensible variation of viscosity during the progress of the change for which an explanation has been suggested. Work also is in progress to examine the limits of the applicability of this method to other reactions both in liquid and gaseous medii.

## 26. Photochemical changes in rubber solutions.

R. K. VALVEKAR and S. K. KULKARNI JATKAR, Bangalore.

Solutions of purified pale yellow crepe rubber in benzene, chloroform, carbon disulphide and cyclohexanol were exposed to diffused daylight and light from a mercury arc in glass and quartz test tubes with control tubes. The viscosities of exposed solutions decreased more rapidly in



quartz than glass tubes and fell nearly to that of the solvent and the solution lost all its adhesive properties after 12 hours exposure to the arc. Experiments are on hand to investigate the nature of change.

27. Condition of sparingly soluble substances when formed in presence of a gel:—Silver Chromate in gelatine from E.M.F. measurements. V.

A. C. CHATTERJI.

Nabar and Desai (*Nature*, April 25, 1931, page 628) from contact potential measurements have come to the conclusion that 95 per cent. of the silver chromate remains in the ionic condition.

From electric conductivity and diffusion experiments (*Trans. Faraday Soc.*, 1926. 72. 23) we have proved that silver chromate remains in the colloidal state like other sparingly soluble salts.

In this paper E.M.F. measurements of cells of the following type were taken to find out the condition of silver chromate in gelatine.

Ag	N/10 Silver nitrate	saturated ammonium nitrate	Silver nitrate, Pot. chromate in gelatine	Ag
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The concentrations of silver chromate, which was formed by the addition of equivalent quantities of silver nitrate and pots. chromate, as well as of gelatine were varied within wide limits.

The results obtained indicate that in the case of silver chromate about 20–40% of the salt is in the ionic state. These results are in agreement with our former conclusion but they do not agree with the conclusion of Desai and Nabar.

Moreover, no decrease in the E.M.F. with time was observed with any of the mixtures, either yellow or red.

In our opinion, the action of gelatine on silver chromate is not different from its action on other sparingly soluble salts as suggested by Desai.

28. Effect of the addition of gelatine having different  $P_H$  values on the precipitation of silver chromate from aqueous mixtures of silver nitrate and potassium chromate.

B. M. NAIK, Bombay.

It is found that a slight increase in the acidity of gelatine increases its inhibitive power considerably and that the quantity of gelatine required to inhibit the precipitation of silver chromate increases with an increase in the concentration of either silver nitrate or potassium chromate.

The results tend to show that silver chromate exists in the ionic condition.

29. Variation of the charge of copper-ferrocyanide sol in the presence of electrolytes and non-electrolytes.

S. G. CHAUDHURY.

Copper ferrocyanide sols prepared by different methods show different cataphoretic speeds. The cataphoretic speed of the sol decreases by partial settling after centrifuging the sol. Also different forms of curves are obtained for the cataphoretic speed of the sol with KCl and  $BaCl_2$  in presence of methyl alcohol and cane-sugar. The results have been explained on the basis of the adsorption theory.



30. Effect of washing and of electrolytes and non-electrolytes on the charge of barium sulphate.

JNANENDRANATH MUKHERJEE, NIRMALAPADA CHATTERJEE,  
and B. NARAYANADAS.

Barium sulphate was precipitated under different conditions and the endosmotic charge on the surface was measured in each case after continued washing.

The effect of different electrolytes such as KCl, HCl,  $H_2SO_4$ ,  $K_2SO_4$  and  $BaCl_2$  and of non-electrolytes such as ethyl alcohol, methyl alcohol and cane sugar solution on the endosmotic charge of heavy spar (natural ore of  $BaSO_4$ ) was observed. In presence of non-electrolytes the positive charge of the powder changed to negative in each case.

The observations are explained on the basis of strong adsorbability of  $H^+$  and  $OH^-$  ions.

31. Coagulation and cataphoretic experiments on arsenious sulphide sol in its relation to the critical potential and influence of ionic environment of the sol on its cataphoretic speed.

JNANENDRANATH MUKHERJEE and S. G. RAJKUMAR.

Measurements of cataphoretic speed of arsenious sulphide sol with  $As_2O_3$ , KCl, HCl, NaCl, LiCl and  $BaCl_2$  have been carried out up to the coagulating concentrations of these electrolytes. In the portion of the speed-concentration curve where the concentration is lower than  $0.1\text{ N}$ , the slope of the curves indicates that the adsorbability of the metallic ions is in the following order,  $Ba > Li > Na > K$ .

At higher concentrations however the slopes of the curves indicate that the adsorbability is in the order  $Ba > K > Na > Li$ . The curve for HCl cuts the other curves and indicates that its relative adsorbability changes with concentration even within this region.

32. The Mechanism of mutual coagulation.

D. C. BAHL, Lahore.

An attempt has been made to determine if there is any precipitation (1) when there is no possibility of chemical interaction between the stabilizing electrolytes, and (2) when the chemical interaction results in the formation of soluble salts and it has been shown that in mutual coagulation the neutralisation of the charge is not the only factor. Chemical interaction between the stabilizing electrolytes (whenever they are present) plays an important part in mutual coagulation.

33. Change of viscosity and electrical conductivity of colloidal solutions on ageing.

D. N. CHAKRAVARTI, Amraoti.

With a view to distinguish between hydrophobe and hydrophile colloids the change of viscosity and electrical conductivity on ageing with respect to the following sols was studied :—

(1) Chromium hydroxide, (2) Ferric tungstate, (3) Mastic, (4) Antimonic acid, (5) Zirconium hydroxide, (6) Gum Dammar, (7) Chromium tungstate, and (8) Antimony sulphide.

It was observed that in the case of hydrophobe colloids the viscosity decreases and conductivity increases on ageing whereas for hydrophile colloids the opposite is true.



## 34. Colloid chemical analysis. Part II.

JNANENDRANATH MUKHERJEE, SATYAPRASAD ROY-  
CHOWDHURY, and AMIYAKUMAR SEN.

It is found in agreement with recent work that the addition of neutral electrolytes to ferric hydroxide and arsenious sulphide sols changes the  $P_H$  of the intermicellary liquid. The  $P_H$  regularly increases with the amount of the sol. Effect of different electrolytes in increasing the  $P_H$  of ferric hydroxide sol is in the order  $K_2SO_4 > KNO_3 > KBr > KCl$ . With arsenious sulphide sols  $KCl$  and  $KBr$  are found to have almost equal effects. With aluminium hydroxide sols it is found that with dilution the cataphoretic speed of the particles of the sol increases at the first dilution (1 : 1) and decreases on further dilution (1 : 5). Concentration of  $Cl^-$  ions,  $H^+$  ion, and total chloride also decrease with dilution.

## 35. Stearic acid hydrosols—An electrometric study.

M. P. VENKATARAMA IYER.

Electrometric titrations of stearic acid hydrosols at different dilutions and at different intervals after mixing with sodium hydroxide solution, have been conducted. Similar experiments have also been repeated with barium hydroxide solution. The marked differences in the nature of the electrometric titration curves in the two cases has been explained from the standpoint of the interchange of ions taking place in the electrical double layer. The absence of a definite stoichiometric relationship between the total acid present, and the alkali required clearly supports the view put forward by Mukherjee that the process of neutralisation takes place by 'adsorption' at the interface. This work is being extended to the 'Colloidal' acids present in the soil.

## 36. Intermicellary composition and stability of ferrocyanide sols.

NIRMALAPADA CHATTERJEE.

Uranyl ferrocyanide, ferric ferrocyanide, cupric ferrocyanide, zinc ferrocyanide, cadmium ferrocyanide and aluminium ferrocyanide sols were prepared in such a way that the intermicellary liquid contained very slight traces of foreign electrolytes. The effect of stabilising electrolytes, of dilution and of hydrogen ion concentration on the peptisation and cataphoretic charge of the above sols were studied. It was found that the charge has got no simple relationship with the phenomenon of coagulation.

## 37. The 'apparent' and 'true' adsorption functions: the study of adsorption of a few binary mixtures by silica gel.

K. S. GURURAJA DOSS, Bangalore.

The forms of the apparent and true adsorption functions are discussed with reference to the results got by some of the previous workers as well as some obtained by the author, working with pyridine-water and carbon tetrachloride-alcohol mixtures. The changes in concentration due to adsorption were measured by means of a Pulfrich refractometer.



38. Studies in the slow coagulation of colloids from the standpoint of Smoluchowski's theory. Part III.

S. S. JOSHI and GURUDAS R. PHANSALKER, Benares.

By employing a method of measuring the degree of coagulation developed previously (Joshi and Prabhu, *Journ. Ind. Chem. Soc.*, 1931, 8, 10, 337) the progress of coagulation of the arsenious sulphide sol has been studied at different temperatures and colloid concentrations. Calculating the Smoluchowski's constant from the equation,

$$\beta = \frac{1}{t} \left[ \sqrt{\frac{v_0}{v_1}} - 1 \right]$$

where the various symbols have their usual significance, it was found that in several series of coagulations smooth regular curves were obtained when  $\beta$  was plotted against  $t$ , the coagulation time, showing a continuous diminution of  $\beta$ . As observed previously (*loc. cit.*) the influence of temperature on  $\beta$  was less than that deduced from the Smoluchowski's theory.

39. On the factors governing the formation and stability of colloidal solutions of sparingly soluble organic acids.

M. P. VENKATARAMA IYER and H. RAMASWAMY IYENGAR.

The formation of colloidal solutions of stearic, palmitic and oleic acids by mixing up with water, solutions of these acids in different organic solvents, and at different temperatures and dilutions has been studied quantitatively. The presence of a polar group in the solvent employed plays a very important part in determining the formation and stability of the colloidal solution. The results are discussed from the standpoint of the surface orientation theory of Langmuir and Harkins. Formation of colloidal solutions by adsorption of constituent ions is discussed and evidence has been adduced to show that the simple mechanism of the colloidal acid ionising partially at the surface and thus conferring stability (as put forward by previous workers) is untenable. Experiments go to show that the stability of the particles is, to a large extent, due to hydration.

40. Studies in some physical properties of gels.

N. A. YAJNIK, D. N. GOYLE, and SHIV LAL.

In the present investigation a systematic study of some of the important physical properties of gels—both of organic and inorganic substances—has been carried out with a view to arrive at some conclusions regarding the structure of these gels.

As a result of this study it has been found that the organic gels show entirely different properties from those of the inorganic gels. The organic gels are more elastic, poorer conductors of sound, more hydrated (or generally speaking more solvated) and more transparent as compared to the inorganic gels.

Further work on the x-ray examination is being carried out and it is hoped that the data taken together with the results of the study made so far will give a fairly good idea of the structure.

41. The refractive index of colloids.

S. S. JOSHI and G. R. GODBOLE, Benares.

During the course of some work by one of us (S. S. J.) to be published shortly, on the variation of the Tyndall beam of colloids during coagulation, the importance of  $\mu$ , the refractive index of the system as by far the



most important variable in the above and allied phenomena was noted. It has been now found in the case of the arsenious sulphide sol that any alterations in the value for  $\mu$  produced by variations in the temperature and the colloid concentration are but slight, viz., of the order of 1-4 in 1000. They are however exceedingly characteristic of the nature and of the stage of the change produced. It has been found in accordance with Paine-Freundlich equations that the time required to produce a given stage of coagulation, as determined by the refractive index of the system, is an exponential function of the coagulator concentration, over a limited though considerable range of the last quantity, and of the colloid concentration. No evidence was obtained which indicated the existence of 'autocatalysis' at any stage during coagulations of even fairly concentrated sols. Results are also given for the variation of the Smoluchowski's constant during coagulations produced under widely varied conditions of temperature, the sol, and the electrolyte concentration.

#### 42. The viscosity of colloids during coagulation.

S. S. JOSHI and K. S. VISHWANATHAN, Benares.

Arising out of an investigation on the viscosity as a measure of the degree of coagulation produced in a colloid, it has been observed that in a number of coagulation-time curves the viscosity diminishes to a minimum during the initial stages of the change, and then increases steadily. The possibility of whether there occurs a preferential adsorption of ions of like charge by the colloid particles during the initial stages has been examined.

#### 43. Organosols of sulphur.

B. S. RAO, Bangalore.

Sulphur sols in organic liquids [Garard and Colt, *J. Am. Chem. Soc.*, 49: 630 (1927)] obtained by the interaction of hydrogen sulphide and sulphur dioxide owe their stability to persulphides of hydrogen whose presence in such solutions has been proved by a new test capable of detecting minute quantities of the persulphides. The inability of certain organic liquids (e.g., alcohol and glycerol) to form sulphur sols by the above reaction is shown to be due to the instability of hydrogen persulphides in such liquids.

#### 44. Solubility of hydrosol sulphur in benzene.

M. R. ASWATHNARAYANA RAO, Bangalore.

The coagulum got by the addition of sodium chloride to hydrosol sulphur (obtained by the action of hydrogen sulphide on sulphurous acid) was refluxed with benzene in Dean Stark's moisture determination apparatus and the effect of this treatment on the solubility at 25°C of the sulphur in benzene determined by a micro-chemical method. The benzene acquired a yellow colour and its sulphur content increased. This effect was probably due to the decomposition of the pentathionic acid present in hydrosol sulphur. Further treatment with fresh benzene gave a low value for the solubility. The hydrosol prepared with sulphurous acid in excess had a far higher solubility than the sol obtained when hydrogen sulphide was in excess.

#### 45. Formation of jellies of hydrous alumina.

K. SUBBA RAO, Bangalore.

The effect of hydrogen ion conc. on the formation of jellies of hydrous alumina was studied by adding sodium aluminate solution and



an equivalent amount of hydrochloric acid simultaneously to Walpole's acetate buffer mixtures. Good jellies were obtained when the  $P_H$  was between 3.7 and 4.3. Below  $P_H$  3.7 the jellies obtained were 'soft' and above  $P_H$  4.3 the jellies were opaque [cf. Prakash and Dhar—*J. Indian Chem. Soc.*, 7: 591 (1930)].

46. The adsorptive capacity of alumina gel.

K. SUBBA RAO, Bangalore.

The effect of temperature of activation on the adsorptive capacity of alumina gel was studied for the range 300° to 1100°C. The water content of the activated gel decreased with an increase in temperature but the capillary space in the gel as determined by the volume of carbon tetrachloride adsorbed per gram of gel was maximum (0.3 c.c.) for the gel activated between 800°–850°C.

47. Adsorption by alumina gel.

K. SUBBA RAO and B. SANJIVA RAO, Bangalore.

Selective adsorption by alumina gel from binary mixtures of benzene with (a) ethyl alcohol and (b) carbon tetrachloride was studied. There is selective adsorption of ethyl alcohol over the entire range, but the 'S' shaped curve is obtained with carbon tetrachloride-benzene mixtures. Silica gel does not give the 'S' shaped curve with the latter. The significance of the difference in behaviour of the two gels is discussed.

48. Effect of the polyvalent stabilising ions on the autocatalytic nature of the coagulation of thorium hydroxide hydrosol.

N. V. KAREKAR and A. M. PATEL, Bombay.

The coagulation velocity of thorium hydroxide sol of different concentrations and dialysed to different extents when coagulated with potassium-, magnesium-, and aluminium-chloride solutions of different concentrations has been studied by a photo-electric cell method.

It is found that for the same concentration of the electrolytes, the coagulation velocity curves become more 'S' shaped with an increase in the valency of the stabilising ion.

49. Effect on the viscosities of thorium hydroxide hydrosol in presence of electrolytes.

N. V. KAREKAR and A. M. PATEL, Bombay.

The changes in the viscosities of thorium hydroxide hydrosol dialysed to different extents, on the addition of varying amounts of potassium chloride, magnesium chloride and aluminium chloride, have been studied.

It is found that with the progress of dialysis the viscosity of the sol increases.

It is also found that on the addition of increasing small amounts of electrolytes, the viscosity first increases and then decreases.

50. Effect of gases on the coagulation of thorium and ferric hydroxide hydrosols.

A. M. PATEL, Bombay.

The effect of coal gas, hydrogen, oxygen, carbon dioxide, nitrogen and acetylene, previously passed through water, when bubbled through thorium



and ferric hydroxide hydrosols containing varying amounts of electrolyte impurities has been studied.

It is observed that all the above gases were effective in bringing about the coagulation of the hydrosols. Carbon dioxide was found to be the best coagulant. It is also found that the amount of the gas required decreases with the increase in the purity of the colloids.

#### 51. Sensitisation of thorium hydroxide hydrosol by non-electrolytes.

P. M. BARVE, Bombay.

The coagulation velocity of thorium hydroxide hydrosol, dialysed to different extents, has been measured by a reliable optical method in presence of potassium chloride as well as magnesium chloride alone and also in presence of potassium chloride with non-electrolytes and of magnesium chloride with non-electrolytes.

It was found that with the progress of dialysis, i.e., with an increase in the purity of the sol, the sol is more and more sensitised by non-electrolytes, such as urea, propyl alcohol.

It is also observed that the sensitisation is less in case of magnesium chloride than in the case of potassium chloride when the sol is impure but with purer samples the difference is not well marked.

#### 52. On the texture of commercial soaps.

P. C. SPEERS, N. A. YAJNIK, D. N. FOYLE, *and*  
ZAFAR-UD-DIN AHMAD, Lahore.

Attempts have been made to investigate the applicability of the various methods to examine the texture of soaps. It has been found that the surface tension considerations play a very important part in determining the texture and appearance of soaps.

#### 53. The saponification of emulsified oils.

P. C. SPEERS, N. A. YAJNIK, D. N. GOYLE, *and* MOHAMMAD SHAFI, Lahore.

Investigations carried out to enquire into the factors governing the saponification of emulsified oils showed that the following play an important rôle in the process of saponification:—

1. The magnitude of the oil-water interface or the degree of emulsification.
2. The total amount of the alkali present.
3. The amount of the oil-phase.
4. The amount of water.

Thus it has been found that the greater the magnitude of the oil-water interface or the degree of emulsification, the greater is the percentage of the oil saponified. The amount of the alkali in the system should be sufficient to saponify the oil present. A greater amount of the oil always lessens the degree of saponification. And lastly the presence of a very large amount of water is injurious to the process.

#### 54. Petrol water emulsions.

B. N. NARAYANASWAMY, S. K. KULKARNI JATKAR, *and*  
H. E. WATSON, Bangalore.

In continuation of previous work on the properties of petrol water emulsions prepared in the premier Colloid Mill, it was found that small quantities of air which were emulsified in the process profoundly modified



the physical properties, especially stability, so as to make the results non-reproducible. The mill was therefore modified to run continuously with one charge so as to trap as little air as possible and the resulting emulsions were found to be very reproducible in various properties such as viscosity, density and stability to temperature and suction. It was further found that both type of emulsions could be prepared beyond the inversion point which is about 32 per cent. petrol when using 5 per cent. of fresh ammonium oleate. The results are discussed from the numerous theoretical view points.

### 55. On the mechanism of unimolecular reactions.

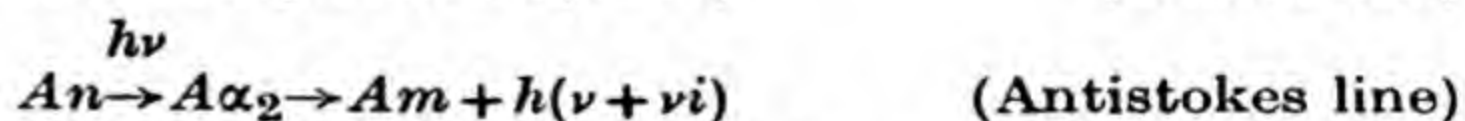
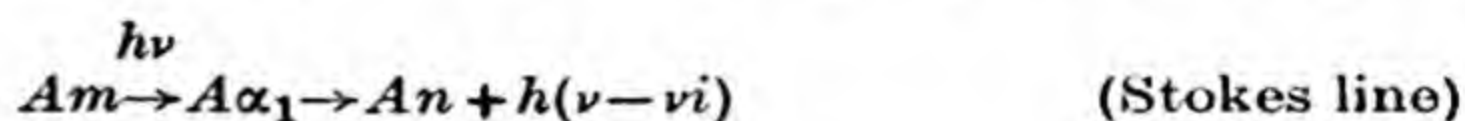
A. GANGULI, Chandernagore.

In a previous paper (*Phil. Mag.*, (1) 12, 583, 1931) expressions for the velocity of unimolecular reactions have been deduced by considering that the molecules are first activated by absorption of radiation followed by the subsequent decomposition of the activated molecules by a mechanism similar to (a) thermal ionisation, (b) desorption. In the present paper the radiation theory as well as the collisional theory are discussed at length, and it is found that none of them is alone adequate enough to explain the observed facts. It is suggested that the energy required (critical increment) for bringing about a thermal unimolecular reaction is derived partly from radiation and partly from collision with surface atoms. The function of radiant energy is merely to loosen the valency electrons (corresponding to the resonance potential) and finally the disruption brought about by collision. The values of 'k' were calculated from the formulæ derived for nearly all available unimolecular reactions and have been found to agree in a satisfactory manner with the experimental values of standard authors. A physical meaning of the effective collisional area (which, in most cases, is identified with the molecular cross-section) is also given. A mechanism of Raman Effect and also of photo-chemical reaction is suggested.

### 56. On the Raman Effect from the standpoint of unimolecular reactions.

A. GANGULI, Chandernagore.

Raman Effect is considered as unimolecular reaction according to the following scheme :



where Am and 'An' represent the molecules in the mth and nth states respectively. The molecule 'An' is regarded as a separate entity and the passage of a molecule from the m→n state is regarded as a chemical reaction involving the absorption of infra-red frequency ν<sub>i</sub>. This is in accordance with the Radiation Theory of chemical reactions as postulated by Lewis and Perrin.

In order to calculate the number of molecules 'N<sub>n</sub>' in the nth state we follow a method due to Christiansen (*Z. Phys. Chem.* 103, 91, 1923) and thus obtain

$$N_n = N_m e^{-\frac{h\nu}{kT}} \frac{kT}{h} \quad \left( \text{for small values of } \frac{h\nu'}{kT} \right)$$

$$N_n = N_m e^{-\frac{h\nu}{kT}} \nu' \quad \left( \text{for large values of } \frac{h\nu'}{kT} \right)$$



Combining this with the radiation density we obtain

$$E_S = N_n \rho_{\nu'} = N_m \frac{k^2 T^2}{h^e} \frac{8\pi \nu'^2}{c^3} e^{-\frac{h\nu}{kT}} \quad (\text{Raleigh-Jeans.})$$

$$E_S = N_n \rho_{\nu'} = N_m \frac{8\pi h \nu'^4}{c^3} e^{-\frac{h\nu}{kT}} e^{-\frac{h\nu'}{kT}} \quad (\text{Wien.})$$

Proceeding similarly for antistokes reaction we obtain

$$E_{AS} = N_m \cdot e^{-\frac{h(\nu-\nu')}{kT}} e^{-\frac{h\nu}{kT}} \frac{8\pi \nu'^2}{c^3} \frac{k^2 T^2}{h^e} \quad (\text{Releigh Jeans.})$$

$$E_{AS} = N_m e^{-\frac{h(\nu-\nu')}{kT}} e^{-\frac{h\nu}{kT}} \cdot \frac{8\pi h \nu'^4}{c^3} e^{-\frac{h\nu''}{kT}} \quad (\text{Wien.})$$

remembering that 'Nn' is obtained by the absorption of  $h\nu_i$

Again since  $\nu' = \nu - \nu_i$  and  $\nu'' = \nu + \nu_i$ , we have

$$\frac{I_S}{I_{AS}} = \frac{E_S}{E_{AS}} = \frac{(\nu - \nu_i)^2}{(\nu + \nu_i)^2} e^{\frac{h\nu_i}{kT}} \quad (\text{for high temp. or small value of } \nu_i.)$$

$$\frac{I_S}{I_{AS}} = \frac{(\nu - \nu_i)^4}{(\nu + \nu_i)^4} e^{\frac{3h\nu_i}{kT}} \dots \dots (\text{for low temp. or large value of } \nu_i.)$$

Thus we see that the intensity is proportional to the square of the modified frequency in one case and to the fourth power in the other case.

This is in accordance with the results of Mandelstan and Landsberg, Orstein and others.

## 57. Kinetics of reactions between ions at great dilutions.

A. N. KAPPANNA and H. W. PATWARDHAN.

A study of the kinetics of the two reactions (1) sodium bromacetate + sodium hydroxide and (2) sodium bromacetate + sodium thiosulphate, has been made at 70°, 80°, and 90°C. in the region of ionic strengths 0.0005 $\omega$ , 0.03 $\omega$ . The salt effect in the first reaction is just the opposite of what is predicted by Brönsted's theory. In the second reaction the Brönsted-Debye theory has been found to quantitatively predict the course of reaction with variation in ionic strength.

## 58. Study of the decomposition velocity of naphthol ethers when heated with halogen acids.

G. B. KOLHATKAR and V. V. BAPAT, Poona.

Concentrated hydrochloric or hydrobromic acid was added to a solution of the ethers in acetic acid and the mixtures then heated on a boiling water bath. The decomposition velocity was ascertained by estimating the naphthols, liberated in the reaction mixture, after a definite interval of time.

The concentration of the halogen acids being about seventeen times that of the ethers, the velocity constants are determined on the assumption that the reactions are unimolecular. The values of the velocity constants obtained are tolerably constant and thus justify the above assumption.



A comparison of the velocity constants reveals the following relations :—

- (1) The decomposition velocity with hydrobromic acid is 1.6 to 1.7 times greater than that with hydrochloric acid.
- (2) The ethers of beta naphthol decompose about 1.8 to 2 times as fast as those of alpha naphthol.
- (3) The decomposition velocities of ethyl and methyl ethers do not show much difference.

### 59. Influence of magnetic field on chemical reactions.

S. S. BHATNAGAR, R. N. MATHUR, and VED PRAKASH.

The influence of a magnetic field on the deposit of copper on iron, when the latter is dipped in a solution of copper sulphate, has been studied. It is found that the amount of deposit in a magnetic field is always greater than that outside it varying with the concentration of the  $\text{CuSO}_4$  solution, and the magnitude of the field. With initially magnetised iron pieces it is however found that the deposit on them is less than on the unmagnetised ones. Similar experiments have been performed on the deposition of silver from a solution of  $\text{AgNO}_3$ , on iron and copper pieces. The results are expected to throw considerable light on the mechanism of this deposition.

### 60. Transportation of metals by electric arc stream.

JITENDRA NATH RAKSHIT.

Electric arcs were produced between pairs of iron and pairs of copper electrodes, and transportation of elements by arc stream were determined per electrochemical equivalent of oxygen liberated by electrolysis, in series with the same circuit, of dilute sulphuric acid.

### 61. Oxidation-reduction potential of a few sulphhydryl bodies.

J. C. GHOSH and S. C. GANGULI.

The discovery of glutathione by Hopkins and the probability of this substance acting as a carrier of oxygen in the living tissues have created considerable interest in the determination of oxidation-reduction potential of sulphhydryl bodies. For cystin-cysteine oxidation reduction, Dixon and Michaelis find that a reversible potential is not attained. The authors find however that if cystine is reduced under anaerobic conditions at a mercury cathode, and the steady potential at the mercury cathode is measured sometime after the electrolysing current is cut off, a thermodynamically reversible system is formed between  $P_H$  6.6 to  $P_H$  9. The E.M.F. is given by the equation

$$E = 0.0793 - \frac{RT}{F} P_H - \frac{RT}{F} \log \frac{[\text{cysteine}]}{\sqrt{(\text{cysteine})}}$$

### 62. Determination of the activity of peroxidases by the measurement of oxidation potentials.

B. B. DEY and M. V. SITHARAMAN, Madras.

It has been shown that the estimation of quinhydrone, formed by the oxidation of hydroquinone, provides a good method of determining the strengths of some of these plant oxidases. It is now found that the change in the concentration of hydroquinone, during its oxidation to quinhydrone by the enzyme, can be accurately followed by measurements of the oxidation potentials of the reversible system quinone: hydro-



quinone, the concentration of the reductant (hydroquinone) varying continuously. A similar observation appears to have been recorded by Stearn and Day (*J. Biol. Chem.*, 1929, 85, 299) who noticed that quinhydrone itself—i.e., the hydroquinone component of it—was oxidised by potato oxidase, there being a rise in potential during the change. A method is now elaborated by which the activities of the enzymes may be studied by noting the changes in potential of the system peroxidase + hydroquinone + gaseous oxygen or  $\text{H}_2\text{O}_2$ : quinhydrone, at constant low temperature.

### 63. Optimal $P_H$ for the activity of peroxidase in *Luffa Acutangula*.

B. B. DEY and M. V. SITHARAMAN, Madras.

One of the interesting results of the experiments now in progress in this laboratory on the oxidising enzymes of plants is the observation that the peroxidase of *Luffa Acutangula* has its maximum activity only in a medium having  $P_H = 6.5$  and this is found to be precisely the value for the  $P_H$  of the normal sap itself. Electrometric measurements of the  $P_H$  of saps of a large number of different samples of the fruit, carried out at a temperature of  $15^\circ\text{C}$ ., have shown that this value remains constant. The  $P_H$  of the medium has been varied from 3.6 to 7.0 by using buffers (a) succinic acid and borax, and (b) potassium dihydrogen phosphate and borax, each buffer mixture being nearly saturated with hydroquinone (1.2 gram hydroquinone per 30 c.c.), and the experiment carried out by mixing 5 c.c. of this mixture with 5 c.c. of the fresh sap, 2.5 c.c. of 2%  $\text{H}_2\text{O}_2$  solution, and 1 c.c. water, allowing the reaction to proceed at  $15^\circ\text{C}$ . for 25 minutes, stopping the reaction by adding 1.5 c.c. of  $\text{N}^\circ\text{HCl}$ , and then estimating the precipitated quinhydrone iodimetrically (cf. *J.I.C.S.*, 1931, 479). The quinhydrone is found to increase steadily from  $P_H$  3.6 to  $P_H$  6.5, after which it falls rapidly.

### 64. Interaction of polybasic acids and neutral electrolytes. Part II.—Tartaric acid.

SUBODHKUMAR MAJUMDAR.

The change in the activity of hydrogen ions of solutions of tartaric acid in presence of different neutral electrolytes like  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{BaCl}_2$  has been followed electrometrically and the thermodynamic dissociation constants calculated. As in the case of phosphoric acid (Part I, *J. Ind. Chem. Soc.*, 1931, 8, 87) the results have been discussed in relation to the Debye theory and factors other than purely electrostatic ones.

### 65. Effect of electrodeless discharge on dye mixtures.

S. S. BHATNAGAR and S. D. MAHANT.

Alizarine and indigo mixed with  $\text{KClO}_3$  do not show any change under the influence of the electrodeless discharge.

Methylene blue and zinc oxide quickly undergo decolorisation under the influence of the discharge, while chlorophyll and zinc oxide paste does not show any change.

Methylene blue and  $\text{CaCO}_3$  show a distinct decolorisation under the action of the discharge.

Methylene blue is unacted upon by the discharge in the presence of mercury vapour.



## 66. Effect of electrodeless discharge on dyes.

S. S. BHATNAGAR and S. D. MAHANT.

Erythrosine, acriflavine, malachite green, alizarine, indigo, chlorophyll, fluorescein, eosine and methylene blue are not affected by exposure to the electrodeless discharge.

Chlorazol Fast, Eosin B (B. D. C.), Chlorazol Fast yellow B. N. Conc. (B. D. C.), Pinachrom, Pinacyanol, Pinaverdol, ethyl cyanine and rhodamin all show a distinctly darker shade after exposure.

## 67. Effect of electrodeless discharge on organic compounds.

S. S. BHATNAGAR and S. D. MAHANT.

Cinnamic acid on exposure to the electrodeless discharge in an atmosphere of oxygen gives a complicated product containing a CO group; this is quite distinct from the ordinary product of oxidation, benzaldehyde.

Resorcinol is unacted upon in the discharge; a mixture of resorcinol and phthalic anhydride exhibits a faint fluorescence after exposure; and a mixture of these two with zinc chloride quickly turns red, showing the formation of fluorescein.

Benzoyl peroxide is not affected by the electrodeless discharge.

## 68. The mechanism of photosynthesis of proteins in plants.

K. S. VARADACHAR, Bangalore.

A preliminary study (Varadachar, *Proceedings of the Indian Science Congress*, 1931) on sunflower plants (*Helianthus annuus* Linn) starved of nitrogen in the soil and injected through the stem with 2 per cent. potassium nitrate solution showed the following characteristics:—

- (1) The plants respond healthily to this treatment.
- (2) There is an increase in Total N.
- (3) There is no definite increase in the amide N and ammonia N.
- (4) The diamino N increases in value.
- (5) The nonbasic N decreases in value.
- (6) There is no accumulation of nitrate.

The present investigation is a more detailed study of the same problem. A comparative study of the effect on protein synthesis of (1) intense respiration and photosynthesis by keeping the plants continuously in bright artificial light, (2) inhibited respiration and photosynthesis by keeping the plants in darkness, and (3) normal conditions of the fields has been followed in the present study.

Analytical data on the plant samples and conclusions drawn therefrom are outlined.

## 69. The photo-chemical reduction of aqueous solutions of silver salts of organic acids.

H. G. DAYAL, J. M. DHAR, and P. S. MacMAHON, Lucknow.

The aqueous solutions of certain silver salts of organic acids were exposed to strong sunlight and the silver reduction-products examined. The salts were found to vary greatly in their behaviour.

Some salts give complex silver sols while others are reduced directly to Ag—Ag<sub>2</sub>O and no sol is formed. Some of the salts on reduction undergo different colour changes, showing progressive alteration in the complexity of the sols. Of the salts so far investigated the sols derived from the tartrate and malate are positively charged, whereas some of the others



as citrate and oxalate, in common with the sol produced from  $\text{Ag}_2\text{O}$  itself on photo-chemical reduction, are negatively charged.

The acetate, malonate, succinate give no sols.

These remarkable diversions are at present under examination, and the nature of the different sols under investigation.

70. The effect of ultra-violet light on the ferrous salts of aliphatic organic acids.

P. LAL and P. B. GANGULY, Patna.

The coagulation by light of Carey Lea's silver sol was explained by us on the basis of a photo-chemical change of ferrous citrate, the stabiliser for this colloid. A further study of the ferrous salts of hydroxy acids has shown that they are generally decomposed on exposure to light. Weighed quantities of pure iron were dissolved in varying quantities of tartaric, citric, malonic, malic, and mucic acids out of contact with air. On exposure, solutions of ferrous citrate and tartarate showed a distinct phototropy. The oxidation-reduction potentials as well as the  $P_H$  values of the solutions were measured before and after exposure. The quantities of ferrous and ferric iron, at different stages of the reaction, were determined by titration with titanium chloride. The  $P_H$  values were found to vary over a fairly wide range. It has been inferred that the iron not only replaces the H in the carboxyl group but also attacks the hydroxyl group.

71. Ignition of oxy-hydrogen gas mixtures in soap bubbles.

HARENDRANATH CHATTERJI, ANATHNATH MITRA, and H. K. SEN, Calcutta.

In continuation of our previous work on the ignition points of explosive mixtures of gases (*J. Ind. Chem. Soc.*, 1929), it has been found that with the increase in the volume of the soap bubbles, the ignition temperature steadily diminishes, till after 350 c.c., it remains constant. A slight but perceptible retardation in ignition, however is noticed. This may be due to the initiation of local catalytic surface combustion leading ultimately to explosion. It may thus be regarded as an example of Hinshelwood's chain reaction. The 1:1 mixture, with the particular platinum point used, ignites at  $245^\circ\text{C}$ ., whilst 1:2 ( $\text{O}_2$ :  $\text{H}_2$ ) mixture ignites at  $273^\circ\text{C}$ . Evidences of the formation of hydrogen peroxide and ozone are noticed in most cases. With the variation in the lengths of the platinum wire, whether in the shape of a point source or in the shape of a spiral source, there is variation in the ignition temperature, the most distinctive feature being that with a spiral source the 1:2 mixture has the minimum ignition temperature whilst the point source gives the minimum ignition temperature with a 1:1 mixture.

72. Synthesis of methane from carbon monoxide and hydrogen in presence of spent sewage.

H. K. SEN and MANINDRANATH MAZUMDAR, Calcutta.

Since the publication of Leiske's work on the conversion of carbon monoxide and hydrogen into methane in the presence of specific bacteria the possibilities of reducing the percentage of carbon monoxide in industrial gases is being explored. A spent sewage which showed no change in the manometer in a closed system for three days was treated with a mixture of one volume of carbon monoxide and three volumes of hydrogen under atmospheric pressure. After four days the mercury thread in the manometer began to rise, whilst after three weeks the rise was 38 cm. The ordinary equation— $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$  would require a contrac-



tion of three-quarters of the total volume. Under the experimental condition, therefore, a conversion of 66 per cent. into methane has been effected. Further experiments are in progress.

73. Synthesis of paraffins from carbon monoxide and hydrogen mixtures.

HARENDRANATH CHATTERJI and H. K. SEN, Calcutta.

By using an iron-copper-alkali catalyst and a 1:4 mixture of CO and H<sub>2</sub>, solid and semi-solid hydrocarbons have been synthesised, using a temperature of 240°C. The exit gas shows the presence of gaseous hydrocarbons to the extent of 6 to 8 per cent. expressed in terms of methane and 8 to 10 per cent. CO<sub>2</sub>. It is therefore usable under boilers. Technical possibilities are discussed.

74. Simultaneous oxidation and dehydration by thoria as catalyst.

B. C. ROY, Calcutta.

In continuation of the work in connection with the preparation of ethyl-aniline, by passing the vapours of ethyl alcohol and aniline over heated thoria, an experiment was conducted by passing air along with the two vapours. After distilling off the ethyl aniline, the tarry residue was extracted with boiling water and on cooling a crystalline substance was deposited. On purifying by recrystallisation from hot water, the substance was found to be acetanilide. The formation of this can be explained by assuming that a part of the ethyl alcohol was oxidised to acetic acid, which by dehydration with aniline produced the acetanilide.

Further experiments regarding the behaviour of thoria as a simultaneous oxidising and dehydrating catalyst is in progress.

75. Interaction between carbondioxide and sulphuretted hydrogen.

M. GOSWAMI and B. C. ROY, Calcutta.

When passed over thoria at 300° a mixture of CO<sub>2</sub> and H<sub>2</sub>S gave methane and sulphur presumably according to the reaction  $\text{CO}_2 + 4\text{H}_2\text{S} = \text{CH}_4 + 2\text{H}_2\text{O} + 4\text{S}$ ; systematic study of this has been done.

76. A method for the purification of coal gas.

M. GOSWAMI, B. C. ROY, and H. N. DAS GUPTA, Calcutta.

The reaction  $2\text{NO} + 5\text{H}_2\text{S} = 2\text{NH}_3 + 2\text{H}_2\text{O} + 5\text{S}$  has been taken advantage of, in purifying coal gas containing definite amount of H<sub>2</sub>S. The aim of the work is to technically utilise the reaction in the purification of coal gas in gas works.

77. Reaction between hydrogen sulphide and sulphur dioxide in non-aqueous solutions.

B. S. RAO and M. R. A. RAO, Bangalore.

Thio-sulphonic acid (thio-sulphurous acid) has been suggested by the authors as the primary product of the reaction between hydrogen sulphide and sulphur dioxide in non-aqueous solutions (*Nature*, 128: 413, 1931). The solutions have been found to contain persulphides of hydrogen. It is suggested that the persulphides are produced by a reversible reaction between thio-sulphonic acid and hydrogen sulphide.

Klein (*J. Phys. Chem.*, 15, 1, 1911) could obtain no correlation



between any physical or chemical property of a liquid and its ability to induce chemical reaction between the two gases. The authors find that the latter property can be correlated with the ability of the liquid to decompose hydrogen persulphide.

78. The reaction between sodium sulphite and sulphur.

S. G. KIRI, K. R. KRISHNASWAMI, and H. E. WATSON,  
Bangalore.

A continuation of the work of Watson and Rajagopalan (*J. Indian Inst. Sc.*, 1925, *VIIIA*, 275).

The reaction was studied employing preparations of sulphur of roughly uniform size, e.g., 60–80 and 100–120 mesh. Comparative estimates of the specific surfaces of the different samples were also obtained by colorimetric measurements of adsorption of Bismark Brown. Although the rate of reaction was found to increase with the surface of the sulphur particles, no quantitative relationship between the two could be established.

79. Alcoholysis of cocoanut oil.

M. GOSWAMI and JAGADANANDA DUTT, Calcutta.

In continuation to the work on alcoholysis published in *J.I.C.S.*, 1931, Vol. 8. P. 413) by Goswami and Ramanujam the following catalysts have been tried:—Phenol-sulphonic acid, Arsenic acid, Phosphoric acid and Glycerophosphoric acid.

80. The formation and dissociation of polyhalides of hydrogen in aqueous solution. 1. Hydrogen chlorobromide.

S. K. ROY, Calcutta.

(Communicated by P. Rây.)

The formation of hydrogen chlorobromide has been studied from the depression of the freezing point of aqueous solutions of hydrochloric acids by the addition of bromine. The equilibrium constant and the heat of reaction have been calculated from the results obtained. (cf. Rây and Sarker, *J.C.S.*, 1922. 1449).

81. Action of nitric acid on tin.

G. S. KASBEKAR, Bombay.

The action of Nitric acid on Tin has been studied,

- (a) by varying the concentration of acid,
- (b) by varying the amount of tin,
- (c) by varying the physical condition of tin,
- (d) by varying the temperature,
- (e) in presence of various catalysts,

in an atmosphere of carbon dioxide. The amount of tin present in the stannous form was determined by iodine titration.

It is found that,

- (1) The amount of stannous salt formed first increases with increase in acid concentration up to a limit and then decreases;
- (2) Increasing the temperature decreases the yield of the stannous salt;
- (3) Percentage of the stannous salt formed from tin-foil is higher than from granulated tin;
- (4) Some catalysts are observed to have a marked effect on the yield of the stannous salt.



82. Period of induction in chemical reactions. Part III—  
Interaction of potassium bromate and hypophosphorous acid.

P. NEOGI and B. N. SEN.

The period of induction has been fully studied with respect to the influences of concentration, temperature, and foreign substances, viz., electrolytes, non-electrolytes and colloids added to the reacting system. The induction period varies inversely as the concentration of each and both of the reactants. The temperature-induction-period curve shows a straight line, the period diminishing with the rise of the temperature. Non-electrolytes like alcohols diminish the period but to different extents, whilst the solvents of bromine cause a more marked diminution in the period with exception of benzene which causes an increase. The colloids and thiosalts considerably diminished the period.

83. Period of induction in chemical reactions. Part IV—  
Interaction of sodium iodate and phosphorous acid.

P. NEOGI and SUDHAMOY MUKHERJEE.

The relations between concentration and the induction period and between temperature and induction period are similar to those obtained in the previous investigation. The alcohols reduced the period considerably and in the case of the two isomeric propyl alcohols the periods are so widely divergent that the reaction may well be used as a test to differentiate the two alcohols. Solvents of iodine markedly reduced the period. Inorganic acids also have considerable influence in causing a diminution in the period.

84. Period of induction in chemical reactions. Part V—  
Interaction of sodium bromate and phosphorous acid.

P. NEOGI and SUDHAMOY MUKHERJEE.

Similar results have been obtained in the course of study of the period of induction in the interaction of sodium bromate and phosphorous acid.

85. On isomeric borohydrates.

R. C. RAY, Patna.

The potassium salt of a borohydrate of the composition  $B_2H_4(OH)_2$  has been described in a previous paper (*Jour. Chem. Soc.*, 1922, 121, 1088-94). Two isomeric compounds of the same composition,  $B_2H_4(OK)_2$ , have been obtained. One is formed by the action of water on magnesium boride, and the other by the action of water on magnesium boride which has previously been mixed with 10 per cent. free boric acid. Hydrogen is evolved from both the isomers when their solutions are acidified with dilute hydrochloric acid, and if the acidified solutions are then treated with standard iodine solutions, a certain amount of iodine is removed in both cases. The ratio of H/I is, however, in one case 2:1 and in the other 1:2. It has not yet been possible to assign constitutional formulæ to the isomeric compounds.

86. On certain monofluophosphates.

H. C. GOSWAMI and PULINBIHARI SARKAR, Calcutta.

Prof. Willy Lange and we have simultaneously discovered the monofluophosphates. We first showed the isomorphism of monofluophosphates



with sulphates. The preparation and properties of the following simple monofluophosphates have been studied, viz : the heptahydrated nickel and cobalt salt—the pentahydrated copper and zinc salt, analogous to the corresponding sulfates. The following double monofluophosphates analogous to the corresponding double sulphates have been prepared, viz., ammonium with nickel and ammonium with cobalt.

The alums corresponding to the sulphate alums were prepared and complete series of mixed crystals with sulphates have been effected.

### 87. Fluoberyllates and their analogy with sulphates. Part II—Fluoberyllates of certain bivalent metals.

NIRMALENDUNATH RÂY, Calcutta.

(Communicated by P. Rây.)

In part I of this investigation it was shown that the fluoberyllate ion ( $\text{BeF}_4''$ ) exhibits a very close analogy with the sulphate ion ( $\text{SO}_4''$ ). The analogy has been found to be most perfect with respect to the solid salts. In the present paper the preparation and properties of the fluoberyllates of some bivalent metals have been described. The salts studied are :

Calcium and strontium fluoberyllates (anhydrous) and nickel, cobalt, zinc, ferrous and copper fluoberyllates (hydrated).

These fluoberyllates resemble the corresponding sulphates not only in their chemical composition but also in their crystalline form, molecular volume, solubility, etc. Fluoberyllates soluble in water have been found to form mixed crystals with the corresponding sulphates.

### 88. Fluoberyllates and their analogy with sulphates. Part III—The Double fluoberyllates.

NIRMALENDUNATH RÂY, Calcutta.

(Communicated by P. Rây.)

Further corroborative evidence of the existence of analogy between the sulphate and the fluoberyllate ion has been furnished by the preparation of a number of double fluoberyllates which resemble the well-known double sulphates of the type  $\text{M}'_2\text{SO}_4, \text{M}''\text{SO}_4, 6\text{H}_2\text{O}$  not only in chemical composition but also in other properties such as crystalline form, molecular volume, solubility, etc. The following double salts have been described :

Hexa hydrated double-sulphato-fluoberyllates of nickel-potassium and zinc-ammonium and hexa-hydrated double fluoberyllates of ammonium fluoberyllate with those of nickel, cobalt, zinc, manganese, cadmium, copper and iron.

These double salts form mixed crystals with the corresponding double sulphates.

### 89. Fluoberyllates and their analogy with sulphates. Part IV—The ammino-fluoberyllates.

NIRMALENDUNATH RÂY, Calcutta.

(Communicated by P. Rây.)

By analogy with the amminosulphates, the ammino-fluoberyllates of silver, copper, zinc, cadmium, nickel and cobalt have been prepared and studied.



## 90. On the complex cyanides of rhenium.

H. C. GOSWAMI and PULINBIHARI SARKAR, Calcutta.

In all its stable salts rhenium is heptavalent. The lower valency rhenium is very unstable. Tetravalent rhenium has been stabilised by forming complex cyanides.

## 91. Some new tetrammine cobaltic complexes and a study of their constitution by means of absorption spectra.

T. DAS GUPTA and PULINBIHARI SARKAR, Calcutta.

The reaction of sodium thiosulphate with cis-diaquo-or transdichloro-tetrammine cobaltic salts has been carefully studied resulting in the isolation of a new series of thiosulphato-aquo-tetrammine cobaltic complexes. Some co-ordination and ionic isomers have been studied. A new method of preparation of the triol-dicobaltic hexammine compounds has been worked out. The constitution of the tetrammine salts has been determined from a study of their absorption spectra.

## 92. Complex compounds of metallic sulphites and thiosulphates with ethylenediamine.

P. NEOGI and HAMID HOSSAIN.

Complex Compounds of thiosulphates and sulphites of cobalt, nickel, zinc, chromium, cadmium, and some other metals with ethylenediamine have been obtained and their constitution determined.

## 93. Complex compounds of metallic hypophosphites, nitrites and arsenites with ethylenediamine.

P. NEOGI and MOHINI NATH PHUKAN.

Complex compounds of metallic hypophosphites, nitrites and arsenites with ethylenediamine have been prepared and their constitution determined.

## 94. Salts of thiosulphato pentacyano cobaltic acid.

S. N. MAULICK, Calcutta.

(Communicated by P. Rây.)

Thiosulphato pentacyano cobaltic acid, and its alkali- and alkaline earth salts have already been described (Rây, *J. Indian Chem. Soc.*, 1927, 5, 325; Rây and Maulick, *Zeit. anorg. Chem.*, 1931, 199, 355). The present paper deals with the preparation of a number of metallic and metal-ammonium salts. Beryllium (basic), manganese, manganese-potassium, silver, silver-ammonium, di- and tetra-ammonium copper, di- and tetra-ammonium zinc, and di- and penta-ammonium nickel salts have been studied.

## 95. Compounds of hexamethylene tetramine with complex cobalt salts and the nature of residual affinity.

PRIYADARANJAN RÂY and MUNINDRA NATH BUXI, Calcutta.

A large number of molecular compounds of hexamethylene tetramine with various salts of thiosulphato pentacyano cobaltic acid have been prepared, and the number of water molecules contained in these molecular compounds are compared with those present in the original complex salts. The difference in hydration, observed in this case, as well as in many



other cases previously examined by other investigators, throws considerable light on the nature of residual affinity.

96. Substituted complex cyanides of cobalt and the influence of substitution on the properties of complex ions.

PRIYADARANJAN RÂY and S. K. CHACKRABARTY, Calcutta.

Metallic salts of an entirely new type of substituted complex cobaltic acid—disulphito tetracyano cobaltic acid—have been prepared, and the constitution of the complex anion is established by various physical and chemical methods. The mobility and the radius of this new complex ion as well as those of the thiosulphato pentacyano cobaltic ion have been determined. From a comparison of the ionic radii of the simple and complex ions of cobalt, some idea about the stability and the strength of the complex ions has been deduced.

97. The estimation of potassium by the cobaltinitrite method.

S. D. SUNAWALA and K. R. KRISHNASWAMI, Bangalore.

The method yields good results only when the relative concentrations of the reactants lie within narrow limits. The precipitates obtained under varying conditions were completely analysed, and the conditions suitable for obtaining  $K_2Na Co (NO_2)_6 \cdot H_2O$  in a pure state were studied. The data obtained enable the determination to be made with an accuracy of about 1 per cent.

98. Quinaldinic acid as an analytical reagent. Part I—Estimation of copper, cadmium and zinc, and the separation of copper from cadmium.

PRIYADARANJAN RÂY and M. K. BOSE, Calcutta.

Various metallic salts of quinaldinic acid have been prepared and their composition and properties studied with a view to determine their applicability for analytical purposes. Copper is completely precipitated in dilute mineral acid solution, whereas zinc and cadmium are quantitatively thrown down from dilute acetic acid and neutral solution respectively. The precipitate formed are highly crystalline and can be very rapidly filtered in a Gooch crucible. Copper, zinc and cadmium have been estimated with excellent results. A quite accurate, rapid and satisfactory method has been developed also for the quantitative separation of copper from cadmium.

99. Chemical examination of some vanadiferrous ilmenites of India.

NIRMALENDUNATH RÂY, Calcutta.

(Communicated by P. Rây.)

Vanadium was discovered a century ago in certain Taberg (Småland) iron ore. Certain ilmenites have been found to contain traces of vanadium. The author has recently examined a few specimens of Indian ilmenites which are characterised by their high percentage (5%) of vanadium. Complete chemical analysis has been done and its composition determined.



100. The chemical and spectrographical examination of some columbites of Gaya.

H. C. GOSWAMI and PULINBIHARI SARKAR, Calcutta.

The Gaya columbites are feebly radio active due to the small amounts of uranium and thorium present in them. A complete chemical analysis of the mineral has been made and a detailed accurate method has been worked out for the analysis of this type of minerals as the methods hitherto adopted are all faulty. Rhenium has been found and has been extracted from 3 kilos of the mineral.

101. The analysis of mixtures of the pentoxides of tantalum and niobium.

D. S. NARAYANA MURTHI, K. R. KRISHNASWAMI, and  
H. E. WATSON, Bangalore.

None of the methods in common use was found to be rapid or simple. The method outlined by Ruff (*Z. anorg. Chem.*, 1926, 156, 215) but left undeveloped has been studied by us in detail and found to be entirely satisfactory.

The method is based on the observation that when heated in a stream of hydrogen, niobium pentoxide is quantitatively reduced to niobium tetroxide, whereas tantalum pentoxide remains unaffected.

102. Note on the filling of nanometers.

M. Q. DOJA.

An improved method for the filling of manometers has been devised. This gets over the difficulty of elaborate sealing which is necessary in the filling of the usual vacuum filled manometers. It also gives a much stronger sealed end than is possible to obtain in the other method, because the sealing is done before the mercury is introduced into the manometer. The method is simple and consists only in introducing pure dry mercury into the evacuated manometer by means of a suitable apparatus which has been described.

103. Action of hypochlorous and other acids on di-isobutylene.

M. L. SHROFF, Benares.

Di-isobutylene was prepared by condensing tertiary butyl alcohol by means of sulphuric acid. A study of the addition products of di-isobutylene with hypochlorous acid, chlorine monoxide, and sulphuric acid was made. Instead of a chlorhydrin, an unsaturated chloride of the empirical formula  $C_8H_{15}Cl$  was obtained, Chlorine monoxide gave a complex mixture of chlorine compounds whereas with concentrated sulphuric acid higher polymers of di-isobutylene were obtained.

104. A preliminary note on the production of oxalic acid from sandal wood dust.

B. H. IYER, Bangalore.

Sandal dust obtained after the removal of the essential oil is being tried as raw material for the production of oxalic acid. The quantitative estimations carried out so far show that 45 per cent. (on the weight of sun-dried dust) of oxalic acid is formed by fusing the dust with alkali at  $200^\circ$  for two hours. The optimum conditions are being worked out and



the real isolable oxalic acid being estimated with a view to see if oxalic acid could thus be profitably produced.

This dust when extracted yielded to petrol 2.5 per cent. of a dark resinous substance which gave an alcohol-insoluble substance as also a bromo-derivative. All these products are under investigation.

105. The fatty acids of 'Ben' oil.

P. RAMASWAMI AYYAR and V. C. PAREKH, Bangalore.

These were separated and esterified by the usual methods and have been found to consist of Myristic (7.3 per cent.), Palmitic (4.2 per cent.), Oleic (65.8 per cent.), Stearic (10.8 per cent.), Behenic (8.9 per cent.), and Lignoceric (3.0 per cent.) acids. The Behenic acid has been proved to be the normal one by direct comparison with a specially synthesised specimen.

106. The fatty acids of Mysore 'Chrysalis' oil.

P. RAMASWAMI AYYAR and V. C. PAREKH, Bangalore.

These have been shown to consist of Palmitic (13.5 per cent.), Stearic (4.0 per cent.), Oleic (33.8 per cent.), Iso-linoleic (38.2 per cent.), and  $\alpha$ -linolenic (10.5 per cent.), and an unidentified lower fatty acid.

107. Studies in the synthesis of higher fatty acids. Part V.

V. A. PATWARDHAN and P. RAMASWAMI AYYAR, Bangalore.

The action of sodium on 11-Bromo-undecylic methylic ester has been studied.

108. Studies in the synthesis of higher fatty acids. Part VI  
—The reactivity of higher alkyl iodides with magnesium.

P. RAMASWAMI AYYAR and V. C. PAREKH, Bangalore.

The yields of Grignard reagents from six alkyl iodides from  $C_{12}H_{25}I$  to  $C_{22}H_{45}I$  have been determined, and incidentally, two new hydrocarbons  $C_{40}H_{82}$  (m.p.  $79-81^\circ$ ) and  $C_{44}H_{90}$  (m.p.  $83-85^\circ$ ) have been synthesised.

109. Studies in fish oils. Part III—Study on the constitution of certain unsaturated fatty acids characteristic of fish oils.

K. D. GUHA, Bangalore.

A sample of Scottish cod-liver oil was used as a source of fatty acids. The acetone-lithium salt separation of the fatty acids and subsequent distillation of their methyl esters were used for the separation of individual acids. The position of double bonds in  $C_{16}$ ,  $C_{18}$ ,  $C_{20}$  and  $C_{22}$  acids with varying degree of unsaturation were studied.

110. Action of alkylene bases on esters.

M. N. RAMASWAMI and P. C. GUHA, Bangalore.

In connection with some other work being done in this laboratory we had occasion to try the action of ethylenediamine on acetoacetic ester. Mason (B. 20, 267) considered the product of the reaction to be ethyl ethylene-di- $\beta$ -amido- $\alpha$ -crotonate and claimed that he obtained the corres-



ponding free acid by heating either the crotonate with water or by heating acetoacetic ester in a sealed tube with ethylenediamine. We have been unable to confirm these results.

This leads us to suspect whether the product of the reaction was really what it was represented to be. The present paper embodies the results obtained by the action of alkylene bases on esters in general and experiments conducted to find the constitution of the resultant products.

### 111. Extension of Michael's reaction. Part IV.

T. N. GHOSH and P. C. GUHA, Bangalore.

In the proceedings of the last year's *Indian Science Congress*, the condensation of phenylazocarboxylic ester, azodicarboxylic ester with the sodium derivatives of acetoacetic ester, etc., was reported. In continuation of the same work, carbethoxythiocarbimide  $\text{COOEt}-\text{N}=\text{C}=\text{S}$  has been found to react with the sodium derivatives of cyanacetic ester, and acetoacetic ester to yield the usual additive products. With malonic ester, however, a compound of the type  $\text{COOEt}-\text{NH}-\text{CS}-\text{CH}-\text{COOEt}$



has been obtained. Mesoxalic-ester-phenylhydrazone  $(\text{COOEt})_2=\text{C}=\text{N}-\text{NHPh}$ , reacting with the sodium derivatives of acetoacetic ester, malonic ester, etc., is simply converted into  $\text{COOEt}-\text{CH}(\text{COOH})-\text{NH}-\text{NHPh}$ . Evidently therefore the expected Michael's condensation has not taken place here, perhaps due to the presence of the positive group  $=\text{N}-\text{NHPh}$ .

### 112. Studies in the acetylation of ligno-cellulose. Part II.

PABITRAKUMAR DAS and H. K. SEN, Calcutta.

The acetylation of cellulose or ligno-cellulose under pressure without the use of any catalyst does not appear to have been undertaken by previous workers. This process was considered to have a peculiar suitability in the determination of the relationship between lignin and cellulose in ligno-cellulose, that is to say whether the two are chemically combined or physically adsorbed. The central idea underlying this view is that if lignin and cellulose are chemically combined and if during acetylation under pressure acetolysis takes place and the lignin is set free from its combination with cellulose, then there should be a new centre for acetylation in addition to the already existing centre for mono-acetylation in the cellulose. A necessary inference from this would be that a modified cellulose, that is to say cellulose isolated from ligno-cellulose by Cross and Bevan's method or chlorine peroxide method or by cuprammonium method would yield under pressure even in the absence of catalysts a diacetyl derivative. This expectation has been realised. There is however an evidence which weakens this theory. It is found in the acetylation of the standard cellulose, cotton itself. Under similar experimental conditions, treated or untreated cotton gave an acetyl value almost nearly agreeing with the monoacetyl. One would be disposed to explain this difference by considering that cotton is a more highly polymerised condition of cellulose. This view is supported by the lower alkali adsorption of cotton in comparison with cellulose from saw dust. To bring all the three under the same category and to explain the inequality in their capacity for undergoing acetylation, one is thus forced to think that this difference arises out of a difference in the degree of polymerisation and the theory that lignin is chemically combined with cellulose loses all force. But to accept that ligno-cellulose which is formed through such a long number of years in the plant world should represent a lower state of polymerisation than cotton is somewhat difficult.

Incidentally acetylation in the presence of sulphuryl chloride,



perchloric acid and limiting quantities of sulphuric acid have been investigated, leading to the establishment of the fact that it is the tri-acetyl derivative alone that gives optically clear solutions. The lower acetates yield only colloidal solutions depending on the size of the particles. The higher the acetylation, the greater the depolymerisation.

Viscosity experiments have been undertaken in this connection.

113. Studies on vegetable proteases. Part I—Protease from *Cicer Arietinum* and *Vigna Catiang*, Endl.

N. DESIKACHAR and C. V. PARAMASIVAN, Bangalore.

Two of the commoner Indian cereals *Cicer Arietinum* and *Vigna Catiang*, Endl. were germinated and the proteases extracted in the usual manner. The preparations were examined (1) for their hydrolysing action on proteins and (2) for their adsorption behaviour by various colloids.

A trial has also been made to aim at the separation of the two existing enzymes, viz., Ereptase and Protease, by adsorption methods.

114. On inulase.

N. KESHA IYENGAR, Bangalore.

Inulase has been prepared from '*Aspergillus* sp.?' by culturing the fungus on an aqueous extract of Artichoke which is found to contain 20 per cent. inulin of the total carbohydrates. After 4-5 days growth, the fungus mat was collected, washed and dessicated in vacuo over sulphuric acid. A grey powder is obtained on grinding the dried material from which an active preparation of the inulase extract is obtained by macerating a given weight of the dry powder with twenty-five times the quantity of toluenated water at room temperature for 24 hours. The filtrate yields an extract rich in inulase but associated with other carbohydrases like invertase and amylase. Various adsorbents are being tried in order to free the extract from other enzymes. A time course study of the inulase extract on inulin at 3.8 P<sub>H</sub> has been completed.

115. On the synthesis of uric acid.

P. C. GUHA, Bangalore.

The present paper is a continuation of previous work (*Proc. Indian Sc. Congress*, 1930, 1931). The action of phenylcarbonate upon ethylene-, oxalo- and glycolyl-diurea as also upon hydantoin acid amide has been studied. The action of urea and biuret upon hydantoin ester NH<sub>2</sub>.CO-NH-CH<sub>2</sub>-COOEt and of urea upon biuret acetamide NH<sub>2</sub>.CO-CH<sub>2</sub>-NH-CO-NH-CO-NH<sub>2</sub> is under investigation.

116.  $\beta\beta'$  Diketo cyclobutanes.

V. M. DIXIT, Poona.

Pechmann (*Ber.*, 1883, 16, 2124 and *Annalen*, 1889, 261, 167) heated citric acid with conc. sulphuric acid to prepare acetone dicarboxylic acid which he condensed with phenols to obtain coumarins. Instead of separating the acetone dicarboxylic acid, he mixed phenols directly with the reaction mixture and later workers have been using the same process for the preparation of the coumarin derivatives.

The author has, however, obtained  $\beta\beta'$  diketo cyclobutane carboxylic

acid  $\begin{array}{c} \text{CO}-\text{CH} \cdot \text{CO}_2\text{H} \\ | \qquad | \\ \text{CH}_2-\text{CO} \text{ (A)} \end{array}$  (m.p. 144°, equivalent 128), (1) by the action of sulphuric acid on citric acid, and (2) by heating acetone dicarboxylic acid

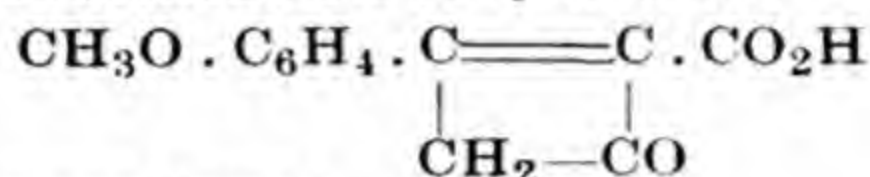


at its m.pt. The new compound being susceptible of hydrolysis to acetone dicarboxylic acid, can only be preserved in sealed tubes.

The new compound gave both mono and di-phenyl-hydrazone, a monoacetyl derivative, a monobromo compound by substitution and a monochloro derivative. The last one gave  $\beta\beta'$  dichloro cyclobutadiene with phosphorus pentachloride.

Elimination of  $\text{CO}_2$  under reduced pressure from (A) gave a substance of the probable formula 
$$\begin{array}{c} \text{CO} - \text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CO} \end{array} \quad (\text{B})$$
 which gives a hydrazone and is converted into  $\beta\beta'$  dichloro cyclobutadiene by phosphorus pentachloride. A compound having the empirical formula of (B) has been obtained by Staudinger (*Ber.*, 1920, 53, 1085).

The acid (A), on condensing with anisol, in sulphuric acid, gave a para substituted cyclobutenone carboxylic acid:—



The work is being continued.

### 117. Formation and stability of a dicyclohexanone.

P. S. MAYURANATHAN and P. C. GUHA, Bangalore.

Condensation of isopropylidene malonic ester and acetoacetic ester was carried out and the constitution of the resulting addition product ( $\alpha\alpha'$ -tricarboxy- $\beta\beta'$ -dimethyl- $\delta$ -keto-ethyl butyrate) and ring-closed product (cyclohexane-1 : 1-dimethyl-3 : 5-diketo-2 : 6-dicarboxylic ester) definitely established by conversion into Vorlander's dilactone and dimethyldihydro resorcin respectively, which were in turn obtained from the addition and condensation products of mesityl-oxide and malonic ester.

On regulated hydrolysis of the ring-closed ester a dicyclohexanone was obtained which presented a new and interesting study of bridge formation and double bonds, their formation and stability, in dimethyldihydro-resorcin. The product is a dehydrated compound of dimethyldihydro-resorcin and definitely establishes the presence of para bonds in phenols.

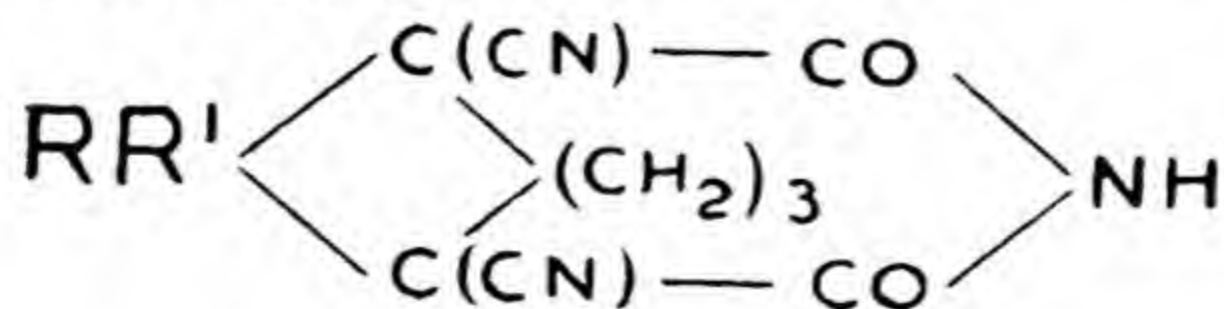
The reactivity and stability of the ring-closed ester towards methylene iodide in presence of sodium was also tried without success. Incidentally, the effect of the gemdialkyl and cyano-groups in the formation of cyclobutane acids was tried. Also the mobility of a tautomeric hydrogen in intermolecular-intramolecular tautomerism was investigated.

### 118. On spiro-compounds. Part II.

P. K. PAUL, Calcutta.

(Communicated by P. C. Mitter.)

With a view to see whether six-membered hydro-aromatic ring systems can associate with six-membered spiro rings, the Guareschi imides from cyclo-pentanone, cyclo-hexanone, 3-methyl cyclo-hexanone and 4-methyl cyclohexanone were condensed with trimethylene bromide following the line of C. A. Kerr (*J. Amer. Chem. Soc.*, 1929, 51, 617) and condensation product of the following type has been obtained.  $\text{RR}'$  being part of different ring systems.





Cyclo-pentane spiro dicyan cyclo-hexane imide, crystallises from acetic acid—m.p. 258°C. Cyclo-hexane spiro dicyan cyclo-hexane imide crystallises from acetic acid—m.p. 204°C. 3-Methyl cyclo-hexane spiro dicyan cyclo-hexane imide, from dilute acetic acid—m.p. 202°C. 4-Methyl cyclo-hexane spiro dicyan cyclo-hexane imide crystallises from acetic acid—m.p. 212°C.

The work is being progressed.

### 119. Attempted synthesis of cantharic acid.

V. N. PAL and P. C. GUHA, Bangalore.

Methyl-cyclohexan-1 : 4-dione-2 : 3-dicarboxylate has been prepared by the reduction of the corresponding dihydroxyphthalic acid. Experiments are in progress to methylate this ester in the 2, 3 positions, and the dimethyl derivative, on reduction of the keto groups and dehydration, is expected to give cantharic acid.

### 120. Curcumone.

N. C. KELKAR and B. SANJIVA RAO, Bangalore.

Curcumone has been obtained by treatment with alkali of a tertiary alcohol  $C_{15}H_{26}O$ . The alcohol yields a mixture of oxalic and p-toluic acids on oxidation with nitric acid. Treatment with sulphur yields an aromatic hydrocarbon. On reduction a saturated alcohol  $C_{15}H_{30}O$  is obtained showing that it is a monocyclic alcohol with two double bonds.

### 121. Examination of the chemical constituents of Swertia Chiratta.

D. N. MAZUMDAR and P. C. GUHA, Bangalore.

The following have been isolated: Stearic, palmitic, cerotic and oleic acid, physosterol, a monohydroxy acid (m.p. 292-93°C), two yellow crystalline phenolic body (m.p. 179-180°C and m.p. 260-61°C), an yellow neutral body (m.p. 196-98°C), a bitter acid called ophelic acid  $C_{13}H_{20}OH_{10}$ , a large quantity of resins and a bitter principle known as chiratin (*Hohn. J.*, 1869, 771) which when boiled with hydrochloric acid is decomposed to ophelic acid and a viscous insoluble substance.

### 122. Constitution of corchoritin. Part II.

N. K. SEN, Dacca.

When corchoritin (*Proc. Ind. Sc. Congress*, 1931) is boiled with alcoholic potash an isomeric lactone ( $C_{12}H_{18}O_3$ ) is formed due to the shifting of the olefinic linking. Confirmation of this is thus afforded by an abortive attempt to isomerise the dihydro-compound with alkali. Corchoritin is readily converted by strong hydrochloric acid into anhydro-corchoritin due to the removal of the hydroxyl group, since while still possessing the lactone group, it yields no longer an acetyl compound. The formation of pyruvic acid by the oxidation of corchoritin proves the presence of the

group  $CH_3-\overset{\overset{|}{|}}{\underset{\underset{|}{|}}{C-C}}$ —as part of the molecule. The immediate reduction of

Tollen's reagent by corchoritin points to the presence of an unsaturated lactone of  $\beta\gamma$ -form. Pyrogenic reduction of corchoritin with zinc dust yields a large volume of gaseous product and a brown semi-solid distillate from which a colourless substance is isolated possessing a characteristic naphthalene-like smell which gives an orange-red picrate melting at 107°.



## 123. Attempts towards synthesis of cantharidin.

B. H. IYER and P. C. GUHA, Bangalore.

The great unstable nature of ortho-dibromo-dimethyl-cyclohexane having yielded only a very meagre quantity of the nitrile (Science Congress Abstracts, 1930, No. 81) synthesis of deoxycantharidin by this method has been suspended.

With a view to see if compounds similar in structure to cantharidin without the two methyl groups, would show vesicant properties, the following reaction has been tried. The disodium salt of di-acetyl-diethyl-adipate reacts with the diethyl ester of dibromo-succinic acid with the formation of 1 : 4-diacetyl-1 : 4-dicarbethoxy-2 : 3-cyclohexanedicarboxylate. Similar reaction with symmetrical dimethyldichlorosuccinic ester is being tried to obtain deoxycantharidin.

Studies in the reactions of di-iodofuran with the sodium salts of malonic-, acetoacetic-, and cyanacetic esters are also in progress.

124. Essential oil from the roots of *Aristolochia Indica* (Linn).

B. L. MANJUNATH, Bangalore.

The pungent smelling oil from the roots of *Aristolochia Indica* was found to possess the following constants:—

$d_{25^{\circ}/25^{\circ}}$  0.9525;  $n_{D 25^{\circ}}$  1.5023;  $[\alpha]_{D 25^{\circ}}$   $-33.11^{\circ}$ ; ester value 7.3; ester value after acetylation 22.5; acid value 2.0.

The oil did not solidify at  $-15^{\circ}$ . When distilled at 1 mm. pressure, boiling commenced at  $90^{\circ}$  and most of the oil came over between  $104^{\circ}$ – $106^{\circ}$ . Distillation stopped at  $148^{\circ}$ . The oil is soluble in 5 volumes of 95 per cent. alcohol.

Substances containing phenolic or the lower alkoxy groups are absent. The carbonyl compounds amount to 3 per cent.

125. Essential oil from the seeds of *Psoralea Corylifolia* (Linn).

H. S. JOIS and B. L. MANJUNATH, Bangalore.

The seeds of *Psoralea Corylifolia* on steam distillation gave a pale yellow oil possessing a strong and persistent odour (yield 0.05%). The oil had the following constants:—

$d_{25^{\circ}/25^{\circ}}$  0.9150;  $n_{D 25^{\circ}}$  1.4906;  $[\alpha]_{D 25^{\circ}}$   $-9.37^{\circ}$ ; acid value 4.6; ester value 12.0; ester value after acetylation 94.3.

The oil partially solidifies and becomes highly viscous when cooled to  $-15^{\circ}$ . The boiling point at 1 mm. pressure ranges between  $70^{\circ}$  and  $152^{\circ}$ . At  $25^{\circ}$  the oil dissolves in half its volume of 90 per cent. alcohol. It is free from phenols and contains 3.2 per cent. of carbonyl bodies.

126. *Dipterocarpus Indicus*. Resin.

N. C. KELKAR and B. SANJIVA RAO, Bangalore.

The oleo-resin examined had the following properties:  $d_{25^{\circ}/25^{\circ}}$  0.9694;  $n_{D 25^{\circ}}$  1.5075, acid value 18.0, saponification value 23.9, saponification value after acetylation 31.8. An acid melting at  $161^{\circ}$  has been isolated and the results of its further examination are described.

127. On an azulene from the oleo-resin of *Dipterocarpus tuberculatus*.

P. C. MITTER and ASOKEKUMAR SEN, Calcutta.

The oleo-resin of *Dipterocarpus tuberculatus* gives on steam distillation about 30 per cent. of sesquiterpenes, boiling between  $100^{\circ}$  and  $105^{\circ}$  at 6 mm.



275 grms. of the oil are fractionated at 9 mm. The physical constants are given below :—

Weight of fraction.	Distillation temperature.	Density. (30 C)	Refraction. (30 C)	Rotation.	$M_d$	$M_d$ for $F_2$
250 grms.	105°–7°	0.9039	1.4967	+11	66.107	
25	113°–5°	0.9114	1.4997	+128	65.82	66.1

The density and molecular refraction agree with that of a bicyclic sesquiterpene.

On dehydrogenation with sulphur a blue oil was obtained which boiled at 135<sub>9mm</sub>. It has a density of 0.9742 at 20°C.

It gave a picrate melting at 120°–121° and a styphnate melting at 106°–7°.

On heating with selenium a similar blue oil was obtained which gave a picrate and a styphnate identical with that given by the blue oil obtained from sulphur treatment.

The physical and analytical data agree with that of Guaiazulene described by Ruzicka and Rudolph. (Helv. c. A. 9, 118, 1926) *Vide Proc. Ind. Sc. Congress*, Lahore, 1927, pp. 161. The work has been resumed with material of guaranteed purity supplied by the Conservator of Forests, Burma.

#### 128. Studies in abnormal optical rotation. Part IV.

S. M. MISTRI and P. C. GUHA, Bangalore.

In continuation of work reported in last year's Science Congress abstract (p. 42, Nos. 143 and 144) it has been found that

- (a) pp-diaminodiphenyl-hydrazodicarbonamide,
- (b) pp-diaminodiphenyl-azodicarbonamide,
- (c) pp-diaminodiphenyl-glyoxal,
- (d) pp-diaminoazobenzene,
- (e) pp-diaminohydrazobenzene,
- (f) pp-diaminobenzil,
- (g) 1:4-diaminoanthracene,

cannot be made to react with camphorquinone under ordinary known conditions due perhaps to the complex nature and high molecular weights of the diamines. One diamine, viz.,  $NH_2.C_6H_4-CH=N.C_6H_4-NH_2$  has been found to react, but even in their case the isolation of the reaction product in a pure form has not so far been successful.

#### 129. Studies in abnormal optical rotation. Part V.

M. S. KOTNIA and P. C. GUHA, Bangalore.

Camphorquinone-mono-hydrazone has been condensed with several aromatic aldehydes containing a system of conjugated double bonds. With the object of studying the effect of two consecutive nitrogen atoms in an unbroken system of conjugated double bonds the compound obtained from acetamino-benzaldehyde and camphorquinone-mono-hydrazone, has been deacetylated and then condensed with a molecule of camphorquinone.

#### 130. On asymmetric synthesis of organic sulphur compounds.

V. C. PAREKH and P. C. GUHA, Bangalore.

In extension of the work published by Guha and Menon (*Ber.*, 1931, 64, 544), another attempt has been made by condensing menthyl- $\beta$ -bromopropionate with methyl ethyl sulphide—but the resulting product on being freed from the menthyl group by hydrolysis has been found to be



inactive. With an object to study the effect of exclusion of the possibility of thetine like ring formation in the unsymmetrical sulphonium compounds the action of *p*-menthylcarboxylate of  $\omega$ -bromacetophenone and menthyl- $\delta$ -brom valerate, etc., on unsymmetrical sulphides is being studied.

### 131. Analysis of Indian coal tars and their distillation products.

S. K. GANGULI and P. C. GUHA, Bangalore.

Coal tars from Calcutta Oriental Gas Company, Bombay Gas Works and Jamshedpur Coke oven have been analysed.

Calcutta Gas Work's tar: (sp. gr. at 23°C, 1.1688) containing free carbon 9.42%; ash 0.067%; yields on distillation under standard conditions, ammonia water 2.50%; light oil (up to 170°C) - 3.20%; middle oil (170-230°C) 12.50%; creosote oil (230-270°C) 10.80%; anthracene oil (270-350°C) 8.20% and pitch 62.80%.

Bombay Gas Work's tar: (sp. gr. at 23°C, 1.1363) containing free carbon 2.55%; ash .12%; yields on distillation under the same conditions ammonia water 4.0%; light oil 8.2%; middle oil 12.5%; creosote oil 10.4%; anthracene oil 10.2%; pitch 54.2%.

Jamshedpur Coke Oven tar: (sp. gr. at 23°C, 1.2400) containing free carbon 17.43%; ash .07%; yields on distillation under the same conditions no light oil, but only 20% of it distils between 230-350°; pitch 80%.

### 132. Examination of the light oil manufactured by Bengal Chemical and Pharmaceutical Works from Calcutta Gas Work's tar.

S. K. GANGULI and P. C. GUHA, Bangalore.

Acids, bases and neutral oils from the light oil are separated and each fractionally distilled with fractionating columns under certain specified conditions and the constituents individually analysed with the following results: ammonia water 0.60%; benzene 7.43%; toluene 7.34%; xylene and other unidentified hydrocarbons in solvent naphtha 6.73%; unsaturated hydrocarbons 1.390%; unidentified hydrocarbons in heavy naphtha 12.18%; pyridine and its homologues 5.57%; phenol 1.34% (by weight); ortho cresol 6.13% (by weight); other higher homologues of the series 7.94% (by weight); naphthalene crude 6.29% (by weight). Hydrocarbons boiling above 200°, 29.14%.

Analysis of the middle oil, creosote oil, anthracene oil and pitch are in progress.

### 133. Chemical investigation of the high boiling bases of heavy anthracene oil.

S. K. GANGULI and P. C. GUHA, Bangalore.

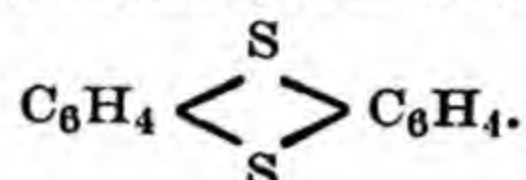
Excepting the isolation of some high boiling bases like di-methyl-quinolines and acridine in the high boiling fractions of the bases obtained from coal tar, no work appears to have been done on the isolation of the bases occurring in anthracene oil. While analysing the acidic, neutral and basic constituents of the different fractions of coal tar distillation products supplied by Bengal Chemical and Pharmaceutical Works, it was discovered that the heavy anthracene oil (B.P. 350° and upwards) contains as much as 25 per cent. bases. The present work embodies the results obtained in the isolation of the ingredient bases by careful fractionation of the products obtained by vacuum distillation under 1 to 25 mm. pressure.



134. Attempts to synthesise diphenylene: isolation of p-diphenylene-di-monosulphide.

V. C. PAREKH and P. C. GUHA, Bangalore.

Turner (*Soc.*, 1915, 107, 1495), Sircar and Majumdar (*J. Indian Chem. Soc.*, 1928, 5, 417) and Menon (Indian Institute of Science unpublished work) made unsuccessful attempts to synthesise p-diphenylene by the action of metals on suitable aromatic halogen compounds. The action of several desulphurising agents has now been tried upon phenylenedisulphide ( $C_6H_4S_2$ )<sub>x</sub> and a compound m.p. 148°, possessing the composition  $C_6H_4S$  and molecular weight 214–218, has been isolated. From its properties it appears to be p-diphenylene-di-monosulphide



Further work on the synthesis of the same and similar other substances from suitable pp-di-derivatives of diphenyl sulphide, -oxide and -imide is in progress.

135. Morellin.

B. SANJIVA RAO, Bangalore.

The acetyl derivative  $C_{38}H_{42}O_{10}$  of this yellow colouring matter gave on oxidation with hydrogen peroxide and potassium permanganate the same acid melting at 49–50°. On reduction a tetrahydro compound was obtained. Distillation over zinc dust yields a hydrocarbon which gives a picrate.

136. Action of chlorine on dilute aqueous solution of some phenols and the effects of the products formed on the taste and odour of water.

B. SANJIVA RAO, Bangalore.

The products formed on gradual addition of chlorine to a dilute aqueous solution of phenol and o-cresol are described.

137. The condensation of resorcinol and secondary alcohols.

J. N. RAY and M. A. HAQ.

Resorcinol condenses with isopropyl alcohol and other secondary alcohols in presence of  $ZnCl_2$  to give products which are analogous to hexyl resorcinol in constitution and antiseptic properties.

138. Substitution in resorcinol derivatives. Chlorination of derivatives of b. resorcyaldehyde.

M. SESA IYENGAR and K. SANTANAM, Bangalore.

A solution of 2-hydroxy-4-methoxybenzaldehyde yields on chlorination under different conditions, the monochloro and the dichloro-aldehydes melting at 107° and 94° respectively. Further, the dichloro-aldehyde forms on treatment with nitric acid a dichloro-nitro-derivative which is identical with the product obtained by chlorinating 6-nitroresorcinol-3-methylether, melting at 102°–103°.

The paper deals with the preparation of the above compounds and their constitution.



## 139. The quarternary salts of p-dimethyl-toluidine.

M. Q. DOJA, Patna.

Several quarternary salts of p-dimethyl-toluidine have been prepared and examined. An improved method for the preparation of trimethyl-p-tolyl-ammonium iodide has been given, and detailed methods of preparation and properties of the others have been noted.

## 140. Studies in diphenylamine derivatives.

R. N. SEN and S. ROY, Calcutta.

Buch (*Ber*, 1884, 17, 2634) obtained diphenylamine in very poor yields by heating aniline and phenol in presence of calcium chloride at 300°. It is now found that a fairly satisfactory yield of diphenylamine (30%) is obtained by the condensation of aniline and phenol in the presence of anhydrous  $\text{ZnCl}_2$  and  $\text{NH}_4\text{Cl}$  in an atmosphere of  $\text{CO}_2$  at 260°. This new method has been worked out for obtaining unsymmetrical diphenylamine derivatives:—Naphthyl-3-amino-4-methyl-phenyl-amine (m-toluylene diamine-b-naphthol-60% yield), 3-amino-4-methyl-3'-hydroxy-diphenylamine (m-toluylene diamine-resorcinol-40% yield), 3-amino-4'-hydroxy-diphenylamine (m-phenylenediamine-hydroquinone), 3-amino-4-methyl-4'-hydroxy-diphenylamine (m-toluylenediamine-hydroquinone).

These diphenylamine derivatives have all been condensed with benzoic acid by heating with  $\text{ZnCl}_2$  to yield unsymmetrical 5-phenyl acridine derivatives. These acridine compounds dye silk with shades varying from orange to deep orange. The fluorescence of these compounds is much more intense than that of benzo-flavine.

## 141. Preparation of p-diethylamino-benzaldehyde.

M. Q. DOJA, and A. MOKEET, Patna.

An improved method for the preparation of p-diethylamino-benzaldehyde by the interaction of diethylaniline formaldehyde and nitroso-diethylaniline has been described. The preparation of nitroso-diethylaniline from sodium nitrite, diethylaniline and hydrochloric acid has also been investigated in this connection, and a technique has been evolved which gives a high yield of the product in a very pure form.

## 142. Studies on azo-aldehydes.

R. N. SEN and B. BANERJEE, Calcutta.

The azo-aldehydes form an interesting group of compounds as intermediate products in the synthesis of useful dyes with multiple chromophores (cf. Green and Sen, *J.C.S.*, 1912, 101, 1113; Dutt, *ibid.*, 1926, 129, 1171; Sen and co-workers, *J.A.C.S.*, 1924, 46, 111; *J.I.C.S.*, 1928, 5, 487; *ibid.*, 1930, 7, 1; *ibid.*, 1930, 7, 151).

The hydroxy-azo-aldehydes described in this paper have been prepared by the application of Riemer and Tiemann reaction on the azo-phenols; the yields of the aldehydes being increased when a dilute solution (23%) of caustic soda is used and a mixture of chloroform and alcohol (1 : 4) is added slowly to preserve the homogeneity of the reaction mixture. The effect of substituents (a) in the phenol residue and (b) in the benzene residue of the azo-phenols on the yield of the aldehydes, has been thoroughly investigated and it is seen that substituents generally exert a more or less inhibiting effect, it being more marked when substituting groups are present in the phenol residue. It is interesting to note that whereas the presence of  $\text{Cl}$ ,  $\text{NO}_2$  and alkyl groups in the phenol residue exerts a strongly adverse influence on the reaction, the influence of these groups in the benzene residue is not however so strong. The constitution



of some of the hydroxy-azo-aldehydes has been proved by their synthesis from coupling corresponding diazotised amines with the corresponding hydroxy aldehydes. These aldehydes generally exhibit marked inactivity in forming bisulphite compounds and they give semicarbazones and phenylhydrazones with extreme difficulty and react with  $\text{NH}_2\text{OH}$  and amino compounds to form oximes and azo-methine compounds respectively.

With a view to study the influence of various substituents, viz.,  $\text{OH}$ ,  $\text{NO}_2$ ,  $\text{CH}_3$ , ( $\text{CH}_3$  and  $\text{C}_3\text{H}_7$ ) some of these aldehydes have been condensed with (a) dimethyl aniline and (b) resorcin to give azo-triphenyl-methane and azo-pyronine dyes respectively with two chromophores in m-positions to each other.

143. Studies in the mercuration of o-, m-, and p-nitrobenzoic acids and 4-nitrophthalic acid.

P. S. MAYURANATHAN and P. RAMASWAMI AYYAR,  
Bangalore.

The mercuric salts of the above acids were dry heated at about  $180^\circ$  and the resulting products were respectively treated with bromine as well as iodine. The following products were, respectively, identified:—

- (1) o-nitro-bromo (or iodo) benzene.
- (2) 2-bromo (or iodo) 3-nitro-benzoic acid.
- (3) 2-bromo (or iodo) 4-nitro-benzoic acid.
- (4) do.

The mechanism of the reactions is discussed.

144. Studies in steric hindrance: Part I.—The isomerism of the monomethyl esters of 3-nitrophthalic acid.

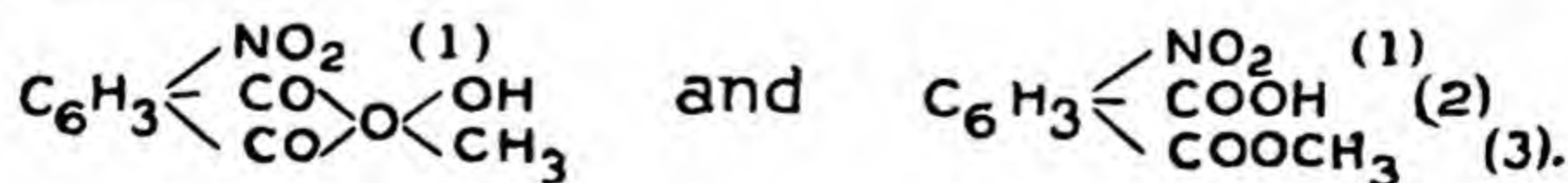
P. RAMASWAMI AYYAR and P. S. MAYURANATHAN,  
Bangalore.

The two monoesters, melting at  $152^\circ$  and  $162^\circ$ , have been prepared by well-known methods and purified thoroughly by a new and a very short method. Their structures had been till now assumed, without adequate chemical evidence, to be  $\alpha$ - and  $\beta$ -monoesters respectively.

Direct evidence for this was sought by dry heating at about  $180^\circ$  of their mercuric salts, followed by halogenation or hydrolysis of the resulting mercurated compounds. In both cases, however, the same products resulted, viz., 2-bromo (or iodo)-3-nitrobenzoic acid, and m-nitrobenzoic acid respectively.

Evidence was also sought by the dry heating of the silver salts and in both cases again only m-nitrobenzoic acid was formed.

Both these evidences point to the fact that the isomerism of the two esters is not due to position and it is suggested that the  $\alpha$ - and  $\beta$ -esters may respectively be



145. 6-Sulpho-salicylic acid.

N. W. HIRWE and M. E. JAMBHEKAR.

p-nitro toluene was sulphonated with fuming sulphuric acid at  $100^\circ$ . 2-sulpho-4-nitrotoluene thus obtained was nitrated with fuming nitric acid, when 2-sulpho-4-6-dinitrotoluene was obtained. 2-sulpho-4-6-dinitro-



toluene was oxidised and 2-sulpho-4-6-dinitro benzoic acid was formed. This compound is finally converted into 6-sulpho salicylic acid by reducing the 6-nitro-group, diazotising and converting into -OH group, and eliminating the 4-nitro-group as usual (by reduction, diazotisation and boiling with alcohol).

#### 146. Thiophthalic acids. Part II.—Nitroderivatives.

G. C. CHAKRAVARTI, Bangalore.

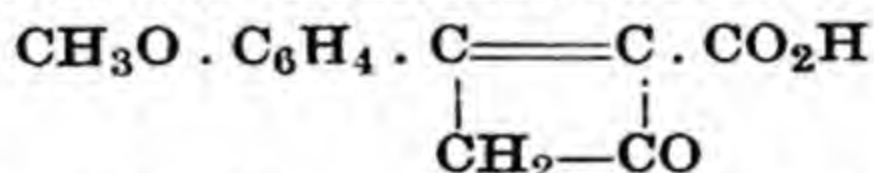
In connection with the syntheses of mono- and dithiophthalic acids I have shown (*J. Ind. Chem. Soc.*, 1928, V, 405) that although mono-thiophthalic acid is very reactive towards oxidising agents yet it can be obtained under certain conditions as a crystalline identity. Dithiophthalic acid, however, is very unstable and cannot be isolated in the free state. Proceeding on the same lines it has been possible to prepare a number of derivatives of nitro-thiophthalic acids. Experiments are being conducted for the isolation of the free acids from these various derivatives.

#### 147. Condensation of phenols and phenolic ethers with acetone dicarboxylic acid. Synthesis of $\beta$ substituted cyclobutenone carboxylic acids.

V. M. DIXIT, Poona.

The author condensed phenol, anisol and o-cresyl methylether with acetone dicarboxylic acid and obtained a series of p-substituted glutaconic acids. (See *Proceedings of I. Sc. Congress*, 1930.)

The primary product in each reaction was, however, found to be an  $\alpha\beta$  substituted cyclobutenone carboxylic acid, the substitution taking place in the para position to the hydroxy or the methoxy group. This compound, on hydrolysis by caustic soda, gave the corresponding glutaconic acid, identical with that mentioned above. Thus, anisol gave



(m.p. 164°, equivalent, 218) which on hydrolysis gave  $\beta$ -4-methoxyphenyl glutaconic acid (m.p. 176° with decomp.). The hydrolysis is so easy that it proceeds in air and in dilute alcohol.

Each of the new cyclic acids gave an isonitroso derivative, anilide, a monochloro compound, a semicarbazone and a mono-acetyl derivative. The last two are titratable acids and can give barium salts.

The new ketonic acids were also obtained from the corresponding glutaconic acids by heating them at their m.pts. and by the action of acetyl chloride or 100 per cent. sulphuric acid.

Further work is in progress.

#### 148. Condensation of phenols with acetone dicarboxylic acid. Synthesis of $\beta\beta$ diphenyl glutaric acids.

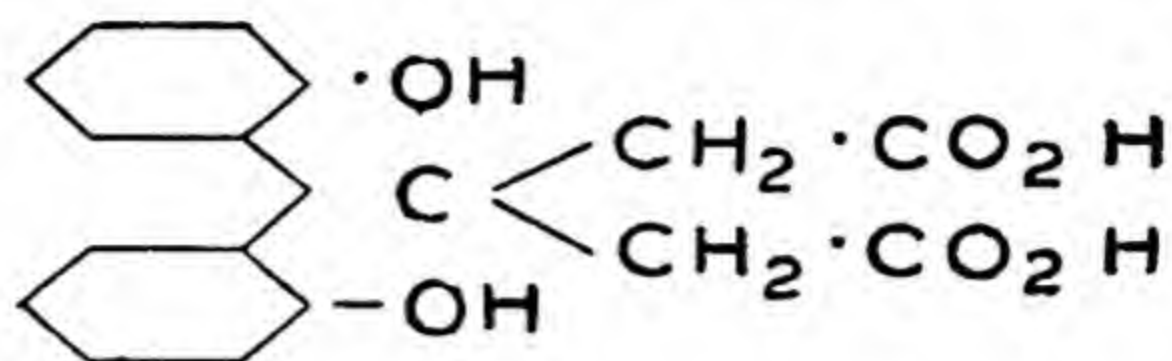
V. M. DIXIT and G. N. GOKHALE, Bombay.

So far, phenols have been condensed with acetone dicarboxylic acid to produce coumarin derivatives (Dey, *Trans. Chem. Soc.*, 1915, 107, 1606) and glutaconic acids (Limaye and Dixit, *Proceedings of the I. Sc. Congress*, 1930), the condensing agent being sulphuric acid.

The authors have found out that two molecules of a phenol condense with acetone dicarboxylic acid to give a new saturated dicarboxylic acid (m.p. 234° decomp.). The equivalent and combustion analysis confer the



formula  $C_{17}H_{16}O_6$  on the compound, to which the following structure has been assigned:—



The new acid also gives a dibenzoyl derivative, a diethyl ester and a diacetyl anhydride with acetyl chloride. On treatment with 100 per cent. sulphuric acid, it is decomposed into phenol and o-hydroxy phenylglutamic acid which is immediately transformed into coumarin-4-acetic acid of (Limaye, *J. I. Chem. Soc.*, 1927, 4, 154).

A series of the new glutaric acids has been obtained by condensing o-cresol, p-cresol and quinol with acetone dicarboxylic acid.

Further work is in progress.

#### 149. $\beta$ —(2-Methoxyphenyl)—glutaconic Acid.

D. B. LIMAYE, Poona.

Limaye and Bhawe (*J. Ind. Chem. Soc.*, 1931, 8, 137) have shown that the product of the direct condensation of anisole and acetone-di-carboxylic acid is  $\beta$ —(4-methoxyphenyl)—glutaconic acid. The corresponding 2-methoxy acid,  $C_{12}H_{12}O_5$ , m.p.  $151^\circ C$ ., also has now been prepared by the methylation of coumaryl-4-acetic acid (Limaye, *J. Ind. Chem. Soc.*, 1927, 4, 159). The new acid has been further characterised by the preparation of anhydride, m.p.  $101^\circ C$ . and semianilide m.p.  $165^\circ C$ . (decomp.). The acid can be readily reduced to be corresponding glutaric acid.

Mr. Gagate (Bombay Univ. thesis, 1931) has prepared a similar glutaconic acid from para cresol and the method which appears to be generally applicable is being extended to other cases and the products used for further synthesis here.

#### 150. Chloralides from $\alpha$ -hydroxy carboxylic acids and their reduction products.

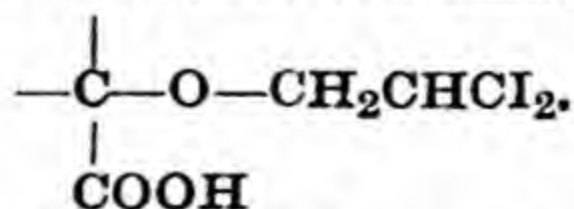
N. M. SHAH and R. L. ALIMCHANDANI, Dharwar.

The condensation of chloral with *m*-cresotic acid led to the synthesis of substances related to  $\alpha$ -coccinic acid (*J.I.C.S.*, 1931, 8, 261).

In order to see whether chloral condenses with *m*-cresotic acid or its derivatives in the *meta* position as claimed by Schleussner and Voswinkel, and with a view to synthesize cochinnilic acid, we tried to condense chloral with 2-methyl-5-carboxy-4-hydroxy-1  $\beta\beta$  dichloro benzene and with 4-hydroxy-5-carboxy-2-methyl mandelic acid and their methyl ethers. The former does not condense at all while the latter gave a product which

proved to be a chloralide  $\begin{array}{c} | \\ -C-O-CH \cdot CCl_3 \\ | \quad | \\ CO-O \end{array}$ . This on reduction with

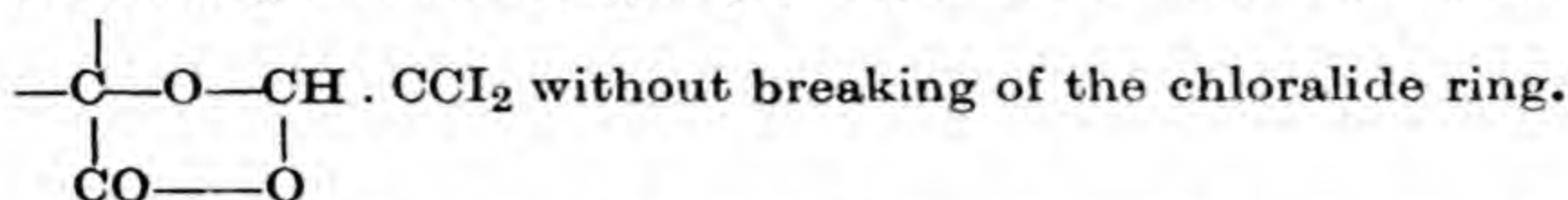
zinc and acetic acid gave a substance containing the group



In aliphatic series, chloralides of tartaric and citric acids show a similar behaviour on reduction: tartaric acid chloralide gave a substance



containing the above groups, while citric acid chloralide is reduced to



The chloralides of other  $\alpha$ -hydroxy acids, e.g., lactic, mandelic and benzillic acids have been studied and their reduction products are under investigation.

151. *m*-(*p*-Dihydroxy) diphenyl phthalide or iso-phenolphthalein.

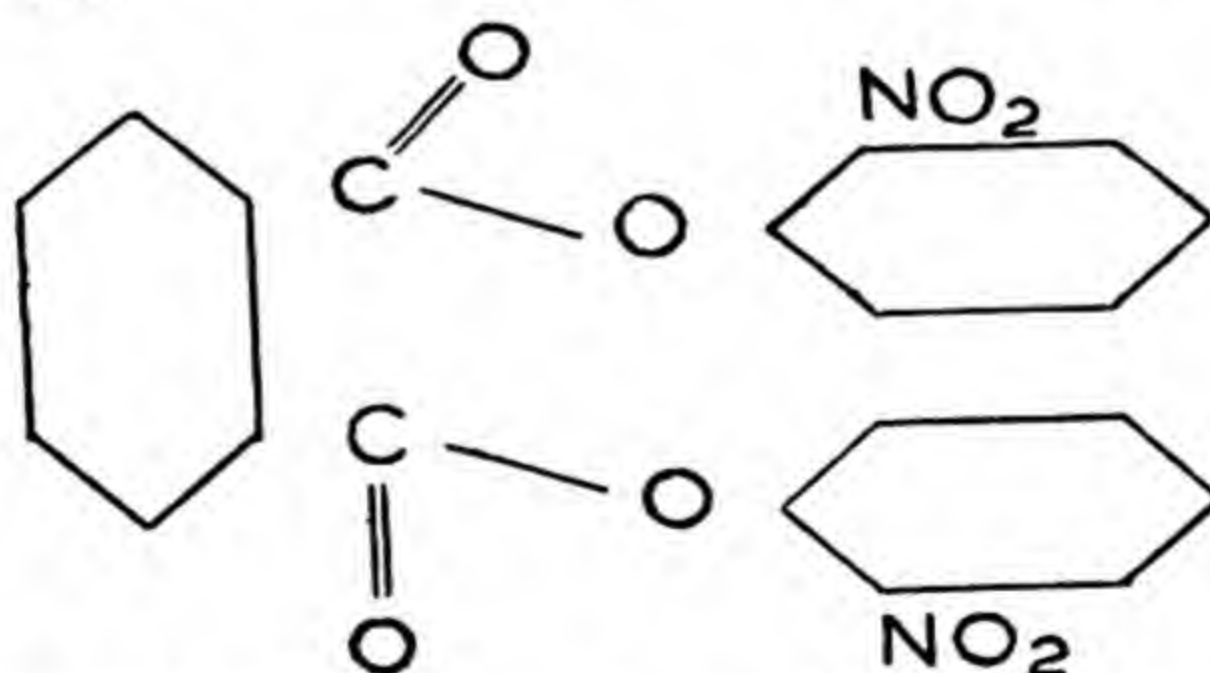
S. Y. KOLHATKAR.

Phenolphthalein and the corresponding ortho compound are known. The meta isomer was prepared by the condensation of phenol with *o*-(*m*-hydroxy-benzoyl) benzoic acid in the presence of zinc chloride as condensing agent. The iso-phenolphthalein is a pink coloured hygroscopic crystalline substance melting at  $60^\circ$  (not sharp) and decomposing at  $80^\circ$ .

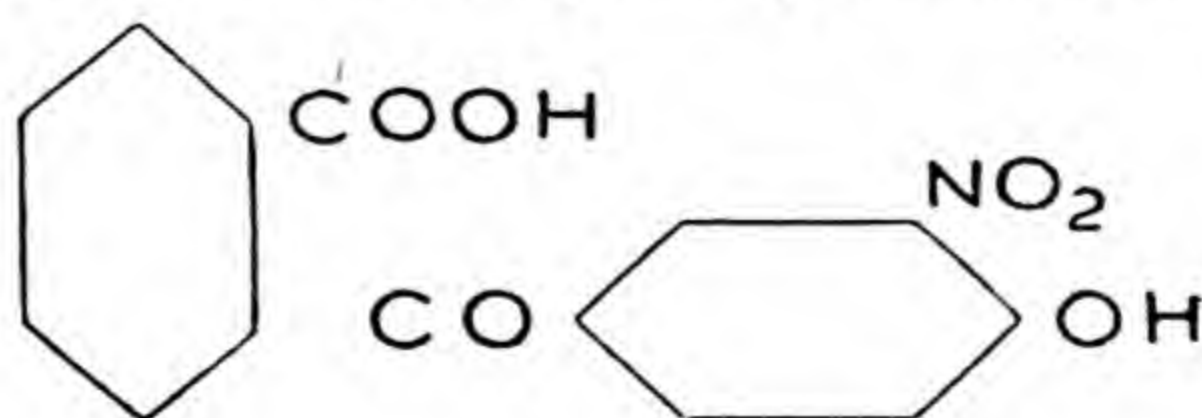
152. Condensation of phthalyl chloride with nitrophenols and their methyl ethers.

S. Y. KOLHATKAR.

By the condensation of phthalyl chloride and nitrophenols in the presence of anhydrous aluminium chloride in carbon tetrachloride, carbon disulphide and acetylene tetrachloride, etc., two types of compounds, viz., phenolic ethers like



and substitution products of hydroxybenzoyl benzoic acid like



were obtained. The latter could also be obtained by the nitration of the hydroxy-benzoyl benzoic acid concerned and so their constitution was confirmed. In presence of aluminium chloride, demethylation of the methyl ethers were found to occur and the products were identical with those obtained with the nitrophenols.



153. Studies in the anthraquinone series : catalytic reduction of anthraquinone derivatives.

P. C. Mitter and DILIPKUMAR BANERJEE, Calcutta.

The chloride of anthraquinone - $\beta$ - carboxylic acid gives on reduction with hydrogen in presence of palladiumised barium sulphate, anthraquinone - $\beta$ - aldehyde. Diacetyl rhein chloride gives on similar treatment the corresponding aldehyde. Further reduction of the aldehydes into the corresponding alcohols with suitable catalysts is being attempted.

154. Colouring constituents of alkanet root.

G. C. CHAKRAVARTI, Bangalore.

In continuation of the investigation recorded previously (cf. *Science Congress Abstracts*, 1930 and 1931) further work has been carried out in obtaining the dyes in the pure state. Two of the constituents, alkannin and anchusin, on analysis give values for their molecular formula which are closely in agreement with those derived from their derivatives. The formula recently suggested for alkannin is criticised.

155. On munjisthin.

P. C. MITTER and HAROGOPAL BISWAS, Calcutta.

When 3-methyl alizarin is treated with sulphuryl chloride in nitrobenzene in presence of iodine, it is converted into 1-2 dihydroxy 3-methyl 4-chloranthraquinone (M.P.  $178^{\circ}$ – $180^{\circ}$ .) On oxidation with nitrous acid in presence of boric and sulphuric acids according to the method of D.R.P. 273341 at a temperature of  $160^{\circ}$ – $165^{\circ}$ , it gives purpurin. Oxidation at a lower temperature— $140^{\circ}$  to  $145^{\circ}$ —gives rise to an acid melting at  $220^{\circ}$ – $222^{\circ}$  (melting point of pseudo-purpurin), but which contains traces of chlorine. From this on reduction with sodium hydro-sulphite and ammonia in the cold, purification over the insoluble barium compound and recrystallisation from dilute acetic acid, munjisthin is obtained. It melts at  $229^{\circ}$ – $230^{\circ}$  and is chlorine-free. On admixture with natural munjisthin it melts at  $227^{\circ}$ – $228^{\circ}$ .

156. Studies in the anthraquinone series :—synthesis of 1, 6 dioxy 3-methyl and 1, 7 dioxy 3-methyl anthraquinones.

P. C. MITTER and NRIPENDRANATH CHATTERJI, Calcutta.

When 4-nitrophthalic anhydride is condensed with meta-cresol in presence of aluminium chloride a mixture of two nitrobenzoyl benzoic acids are obtained, one (A) melting at  $196^{\circ}\text{C}$ . and the other melting at  $202^{\circ}$ – $3^{\circ}$ . On fusion with potash, the acid (A) gave p-nitrobenzoic acid and an acid which gave a violet coloration with ferric chloride, while (B) gave m-nitrobenzoic acid and an acid which also gave a violet coloration with ferric chloride. (A) is therefore 4-nitro-(2'oxy-4' methyl benzoyl) 2-benzoic acid while (B) is 5-nitro (2' oxy-4'methyl benzoyl) 2-benzoic acid. On reduction with ferrous sulphate and ammonia, A gave 4-amino-(2' oxy-4' methyl benzoyl) 2-benzoic acid (m.p.  $218^{\circ}\text{C}$ .) which on diazotisation gave 4-oxy (2'oxy-4' methyl benzoyl) 2-benzoic acid (m.p.  $214^{\circ}$ – $215^{\circ}\text{C}$ .) On heating with boric anhydride and sulphuric acid, this is converted into 1,7 dioxy 3-methyl anthraquinone (m.p.  $255^{\circ}$ – $56^{\circ}\text{C}$ .) Similarly, from the acid (B), 5-amino (2' oxy-4' methyl benzoyl) 2-benzoic acid (m.p.  $237^{\circ}$ – $38^{\circ}\text{C}$ .), 5-oxy-(2' oxy-4' methyl benzoyl) 2-benzoic acid (m.p.  $215^{\circ}$ – $16^{\circ}\text{C}$ .) and 1, 6-dioxy 3-methyl anthraquinone (m.p.  $213^{\circ}$ – $14^{\circ}\text{C}$ .) were obtained.



## 157. Studies in the fluorenone series.

A. C. SIRCAR and K. C. BHATTACHARYYA, Calcutta.

In continuation of the work of the present authors described in the *Journal of the Indian Chemical Society* (1931, Vol. VIII issue No. 9) the present paper deals with a number of substantive cotton dyes that have been prepared from 2 : 7-diamino-fluorenone (Schmidt and others, *Ann.*, 390, 210) by coupling the tetrazo salt with various phenolic and basic constituents.

An improved method of preparing 2-amino-fluorenone (cf. Diels, *Ber.*, 34, 1748) giving much better yield has been described.

2-Iodo and 2-bromo-fluorenone, which had already been prepared before by other ways (Cf. *Anal. Assoc. Quin. Argentina*, 1297, 15, 5-9 and Schmidt and Bauer, *Ber.*, 1905, 38, 746) have now been prepared from 2-amino-fluorenone via diazo-reaction.

## 158. Studies in acenaphthenone.

A. C. SIRCAR and RAJGOPALAU, Calcutta.

Acenaphthenone has been studied through its ' $\text{CH}_2-\text{CO}$ ' group and the following types of compounds prepared. (1) Pirylium compounds; (2) Indole derivatives; (3) Quinoline derivatives; and (4) Azo-methine derivatives. The action of nitroso compounds, and aromatic ortho diketones on acenaphthenone has also been studied.

## 159. Acenaphthene quinone and hydrazine hydrate.

B. K. BANERJEA, Rajshahi.

The action of hydrazine hydrate upon certain ketones and diketones is known. In this paper the action of hydrazine hydrate upon acenaphthene quinone has been investigated. A monohydrazi-compound melting at  $136^\circ-137^\circ$  and its benzaldehyde derivative melting at  $223^\circ$  are described. With two molecules of hydrazine hydrate, instead of obtaining a dihydrazi-derivative, two isomeric compounds styled as (1) acenaphtho-osotriazole and (2) acenaphtho-aziimide are produced, one melting and decomposing at  $225^\circ-226^\circ$  and the other melting at  $175^\circ-176^\circ$  but not decomposing at  $225^\circ-226^\circ$ .

## 160. Dyes derived from pyrazindicarboxylic acid: pyrazindicarboxyleins.

S. C. DE and P. C. DUTTA, Muzaffarpur.

This paper deals with phthalein dyes which were prepared from pyrazin-o-dicarboxylic acid (Gabriel and Sonn, *Ber.*, 1907, 40, 4851) by condensing it with various aromatic amino and hydroxy compounds and were compared with corresponding dyes derived from phthalic anhydride on the one hand and quinolinic acid (Ghosh, *J.C.S.*, 1919, CXV, 1102) on the other. Apparently the intensity of colour of these dyes has been found to be enhanced but the fluorescent property much decreased. Of the compounds, the m-phenylenediamine condensed product has the highest fluorescence. The use of condensing agent such as sulphuric acid zinc chloride, etc., is not essential as even without them condensation takes place.

## 161. Dyes derived from acenaphthoquinone and isatin: Quinoxalo-acenaphthazines and quinoxalo-indazines.

P. C. DUTTA and S. C. DE, Muzaffarpur.

In continuation of the work of De and Dutta on quinoxalophenanthrazines (*Proc. Indian Sc. Congress*, 1931), the action of diaminoquinoxalin



by Bladin (*Ber.*, 1885, 18, 672) on the aromatic ortho-diketones was further studied. The communication deals with compounds produced by the condensation of diaminoquinoxalin with acenaphthoquinone, isatin and their various derivatives. They are all coloured substances ranging from yellow to reddish brown. The compounds are all well-defined crystalline substances characterised by high melting point. They dissolve in concentrated sulphuric acid from which the original substances can be precipitated as a flocculent mass well-suited for dyeing.

162. Vat dyes derived from phenanthraquinone-thionaphthene-phenanthrene indigoes.

P. C. DUTTA, Muzaffarpur.

It has been shown by Friedlander, Herzog and Voss (*Ber.*, 1922, 55, 1591), that phenanthraquinone condenses very easily with hydroxythionaphthene in acetic acid solution containing traces of hydrochloric acid and a violet dye is produced. Later on Pummerer and Luther (*Ber.*, 1931, 64, 831) have obtained that very substance as a red brown crystalline mass by a slight modification of the above method and they say that the original substance as obtained by Friedlander and his collaborators must contain traces of thio-indigo as an impurity. The present author got the substance as a chocolate brown mass and he further extended the reaction by condensing hydroxythionaphthene with various derivatives of phenanthraquinone. The condensation products with bromo and nitro-phenanthraquinones are found to be violet dyes whereas those with amino and hydroxyphenanthraquinones, black or brownish black. The substances dissolve in conc. sulphuric acid with a green, violet green or violet brown colour and the original dyes can be precipitated back by treatment with water which precipitates are found to be quite suitable for dyeing on wool from an acid bath. Except the bromo-compounds, they dissolve in hydrosulphite vat with a yellowish brown colour from which the original dyes are precipitated by oxidation with air.

163. Indole transformation of the pyrrol ketones.

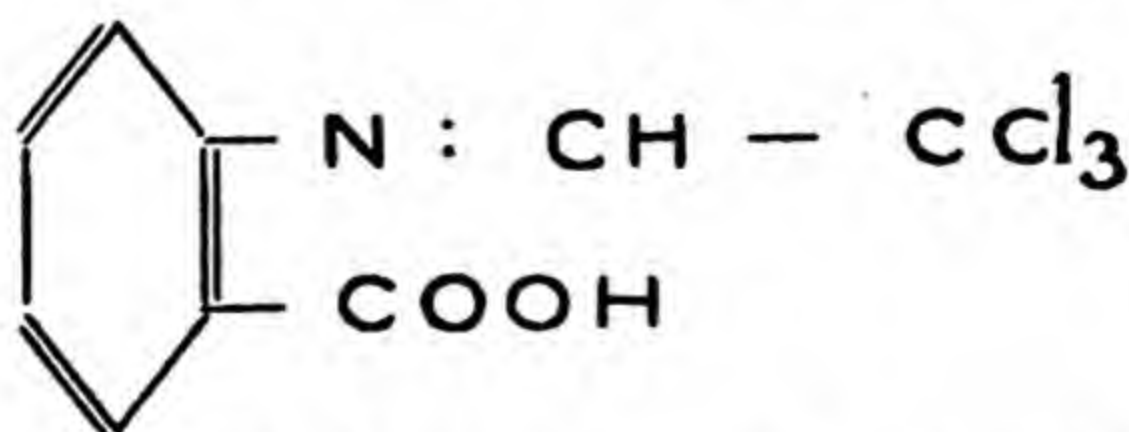
A. U. QUERESHI and J. N. RAY.

A number of pyrrol methyl ketones have been synthesised and converted into pyrindoles. The mechanism of Fischer's indole transformation has been studied. The synthetic pyrindoles may be precursors of tryptophane and proline in the hydrolysis of the proteins.

164. A new synthesis of indigo.

K. S. VAIDYANATHAN.

Anthranilic acid (1 mol.) is condensed with chloral (1 mol.) to give a product (*Vide Ber.*, 1895, 28, 2812, and *J. Am. C.S.*, 1908, 30, 139) of the formula



The acetyl derivative of this product on reduction with zinc and acetic acid gives two products, one in a good yield and the other in small quantities.

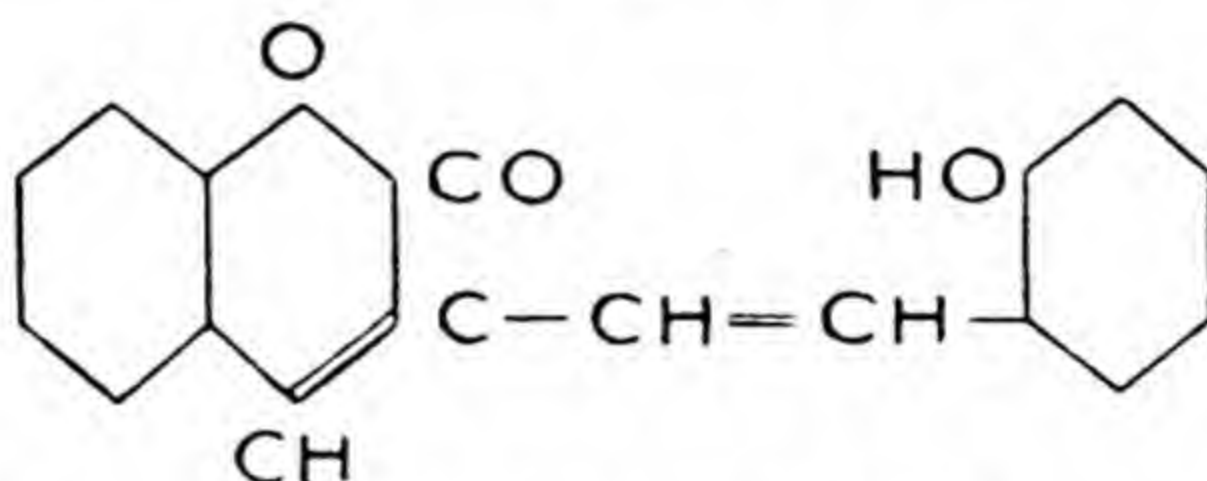


The reduction product formed in larger quantities is fused with sodium hydroxide, diluted with water, and oxidised with atmospheric air, when it yields indigo.

### 165. Condensation of salicyl-aldehyde with sodium succinate.

B. B. DEY and Y. SANKARANARAYANA.

Dyson (*Trans.* 1887, 63) who studied the reaction between salicyl-aldehyde (2 mols.), sodium succinate and acetic anhydride at a high temperature, obtained 3, 3'-dicoumarin as the sole product of the reaction. It is now found that a small amount of coumarin-3, acetic acid is also formed in this reaction if only 1 mol. of the aldehyde is taken : in a typical experiment carried out under Dyson's condition, 0.15 gram of coumarin-3, acetic acid crystallising in yellow plates melting at 158°C (methyl ester, colourless needles, m.p. 77°C.), was obtained from 3 g. of salicyl-aldehyde. If, however, the acetic anhydride be replaced by succinic anhydride, coumarin-3, acetic acid is obtained as the main product of the reaction. The following results were obtained from a typical experiment : 3 g. salicyl-aldehyde, 4 g. sodium succinate and 3 g. succinic anhydride, on heating to 180°C. for four hours, gave 1.2 g. coumarin-3, acetic acid, 1 g. 3, 3'-dicoumarin (m.p. 315°C.), and 0.7 g. of another crystalline product (m.p. 207°C.) soluble in cold alkali but insoluble in alkali carbonate, which, from analyses and chemical behaviour, appears to have the structure given below :—



It forms an acetyl derivative melting at 177°C.

### 166. The coumarin condensation.

V. M. DIXIT and G. N. GOKHALE, Bombay.

Dey (*Trans. Chem. Soc.*, 1915, 107, 1606) obtained coumarin acetic acids by condensing phenols with acetone dicarboxylic acid. In each reaction, he obtained a coumarin acetic acid which changed m.pts. with a change in the solvent of crystallisation. In some cases the m.pt. of the crystallised substance was lower than that of the crude product.

With a view to investigate into the strange phenomenon, the authors condensed phenol and the three cresols with acetone dicarboxylic acid. In each case, two interconvertible compounds were isolated from the crude product. Thus, m-cresol gives a compound (A) (m.p., 168° decomp.) which agrees in composition and properties with 7-methyl coumarin-4-acetic acid and gives 4 : 7-dimethyl coumarin on decomposition at the m.pt.; and another compound (B) (m.p., 210° decomp.) which contains a molecule of water less than (A) and gave also 4 : 7 dimethyl coumarin on decomposition at the m.pt. The mixture of (A) and (B) melts at 180°–190° decomp.

(A) can be converted into (B) by 100 per cent. sulphuric acid and hydrolysis by NaOH promotes the reverse change which can proceed of its own accord in air and in dil. alcohol. Similiar pairs of definite compounds showing clear differences in equivalents and analysis have been obtained from each of the other phenols mentioned above.

The work is being continued.



## 167. Introduction of arsenic in substituted coumarins.

M. GOSWAMI and H. N. DAS GUPTA.

Substituted amino coumarins have been converted into corresponding arsenic acids by means of Bart's reaction.

## 168. 5-Amino-ortho-coumaric acid.

R. N. SEN and B. BANERJEE, Calcutta.

The diazo-transformations of 5-amino-ortho-coumaric acid are described in this paper. 5-amino-ortho-coumaric acid (m.p. 194°) has been obtained by the reduction (with iron and hydrochloric acid) of 5-nitro-ortho-coumaric acid which is readily obtained in quantity from 6-nitro-coumarin (Sen and Chakraverti, *J. Indian Chem. Soc.*, 1930, 7, 247).

169. 6-Aldehyde-4-methyl- $\alpha$ -naphtha-pyrone.

R. N. SEN and G. MUKHERJEE, Calcutta.

6-aldehydo-coumarin was previously obtained by the application of Reimer and Tiemann's reaction on coumarin (Sen and Chakraverti, *J. Am. Chem. Soc.*, 1928, 2428). 4-methyl- $\alpha$ -naphtha-coumarin (pyrone) similarly yields about 30 per cent. of an aldehyde, the aldehydic group entering the 6-position (para to original OH group), there being no other possibility. The aldehyde does not melt up to 300°, readily gives a phenyl hydrazone (m.p. 125°), a semi-carbazone (m.p. 260°) and an oxime (which does not melt up to 260°).

The aldehyde condenses with dimethyl aniline and o-cresotinic acid to produce triphenyl methane dyes (lenco); which on oxidation produce respectively a bluish-green shade and a golden yellow shade on silk and wool. A pyronine dye has been obtained by condensing the aldehyde with four molecules of resorcinol, when the CO group in the lactone ring as well as the aldehyde group react. Silk is dyed a bright orange shade by the sodium salt of this compound.

170. The condensation of  $\alpha$ -formylphenylacetonitriles with phenols.

I. C. BADHWAR and K. VENKATARAMAN.

With Baker and Menon we have shown (*J.C.S.*, 1931) that the Hoesch reaction of  $\alpha$ -formylphenylacetonitrile (I) with resorcinol, phloroglucinol and orcinol takes an abnormal course and leads to the coumarin in every case. The present work concerns the condensation of (I) with hydroxy-hydroquinone triacetate (II),  $\alpha$ -naphthol (III) and  $\beta$ -naphthol (IV). (II) gave a mixture of products of which the expected coumarin or isoflavone was not one; for comparison, 6 : 7-dihydroxy-3-phenyl-coumarin was prepared by treatment of (II) with oxymethylene phenylacetic ester and sulphuric acid. (III) gave 3-phenyl-1 : 2- $\alpha$ -naphthapyrone. Two substances were obtained in the case of (IV); one was identical with the product of the action of sodium phenyl acetate and acetic anhydride on 2-naphthol-1-aldehyde; the other is probably 3-phenyl-1 : 2- $\beta$ - $\beta'$ -naphthapyrone.

## 171. Chromones derived from 2-phenylacetyl-1-naphthol and 2-benzylacetyl-1-naphthol.

U. S. CHEEMA and K. VENKATARAMAN.

2-phenylacetyl-1-naphthol (I) and 2-benzylacetyl-1-naphthol (II) have been made by the Nencki reaction—heating  $\alpha$ -naphthol with acid and



zinc chloride. (I) and (II) undergo Robinson's chromone condensation readily. 2-Methyl-3-phenyl-1 : 4- $\alpha$ -naphthapyrone (III), 2 : 3-diphenyl-1 : 4- $\alpha$ -naphthapyrone (IV), 2-methyl-3-benzyl-1 : 4- $\alpha$ -naphthapyrone (V) and 3-benzyl- $\alpha$ -naphthaflavone (VI) have thus been prepared. (III), (V) and (IV) were reported to have been made by Jacobson and Ghosh (J.C.S., 1915, 1916) by condensing  $\alpha$ -naphthol with  $\beta$ -ketonic esters; but their compounds are shown to be coumarins. (I) did not react with ethyl formate and sodium; (II) gave a mixture of 3-benzyl-1 : 4- $\alpha$ -naphthapyrone and 2-hydroxy-3-benzyl- $\alpha$ -naphthapyranone.

## 172. 2-Styrylchromones.

U. S. CHEEMA, K. C. GULATI, and K. VENKATARAMAN.

The action of cinnamic anhydride and sodium cinnamate on resacetophenone, phloracetophenone and 2-acetyl-1-naphthol gave amorphous products from which no pure styrylchromone could be isolated. Respropionophenone, 2-propionyl-1-naphthol, 2-phenylacetyl-1-naphthol and 2-benzylacetyl-1-naphthol, however, reacted readily with cinnamic anhydride and with p-methoxycinnamic anhydride giving 3-substituted 2-styrylchromones. Two other possible methods for the preparation of styrylchromones unsubstituted in the 3-position were investigated. The first was to condense ketones such as o-hydroxyacetophenone with cinnamaldehyde, convert the cinnamylideneacetophenone to the 2-styrylchromanone and then treat the latter with phosphorus pentachloride; the chromanone change did not proceed. The second method was a re-examination of that due to Heilbron, Barnes and Morton and consisted in the condensation of 2-methylchromones with aromatic aldehydes. The process was found to be much more generally applicable than Heilbron and others considered and numerous 2-styrylchromones and 2-styrylnaphthapyrones have thus been prepared. The synthesis of certain 2-styrylchromones, having a possible bearing on the constitution of plant pigments such as fukugetin and pratensol, is in progress.

## 173. $\alpha$ -Naphtha- $\gamma$ -pyrones.

K. S. KANG and K. VENKATARAMAN.

Bhullar and one of us having shown earlier (J.C.S., 1931) that the action of acid anhydrides on 2-acetyl-1-naphthol (I) leads to a mixture of naphtha- $\gamma$ -pyrones and their 3-acylated derivatives difficult to separate, further naphthapyrones have now been made by the chalkone method. The condensation of (I) with o-methoxybenzaldehyde and 3 : 4 : 5-trimethoxybenzaldehyde respectively gave the corresponding 2-benzylideneacetyl-1-naphthol; treatment of the acetate with bromine yielded the dibromide, which was then treated with alcoholic potash. 2'-Methoxy- $\alpha$ -naphthaflavone and 3' : 4' : 5'-trimethoxy- $\alpha$ -naphthaflavone thus obtained, were then demethylated to the corresponding hydroxy-compounds whose reactions and dyeing properties are recorded.

## 174. Condensation of acetone-di-carboxylic acid with paracresolmethylether.

D. B. LIMAYE and G. R. GOGATE, Poona.

It has been shown by Limaye and Bhawe (J. Ind. Chem. Soc., 1931, 8, 137) that when anisole is condensed with acetone-di-carboxylic acid  $\beta$  (4-methoxy phenyl)—glutaconic acid is produced. It seemed of interest to investigate a case where the para position is already occupied.

The condensation with paracresolmethylether has yielded under suitable conditions four products :

(a) the already known coumaryl-4-acetic acid from paracresol



- (b) a dibasic acid— $\beta$  (2-methoxy-5-phenyl) glutaconic acid,  $C_{13}H_{14}O_5$ , m.p.  $169^\circ C$  (decomp.)
- (c) a monobasic acid-3-keto-4-methyl-7-methoxy-hydrindenylidene-acetic acid,  $C_{13}H_{12}O_4$  m.p.  $218^\circ C$  (decomp.) and
- (d) a high melting acid of unknown constitution which gives (c) on heating with sulphuric acid.

Treatment of (a) with methyl sulphate gives (b) which as a  $\beta$  substituted glutaconic acid gives an anhydride m.p.  $117^\circ C$ , titrating as a monobasic acid, an acidethylester, m.p.  $82^\circ C$ , a semianilide m.p.  $146^\circ C$ , an anil m.p.  $225^\circ C$  and other derivatives.

The constitution of (c) is supported by its formation from (b) by elimination of water, production of the appropriate phthalic anhydride, m.p.  $186^\circ C$  on oxidation, formation of a semicarbazone m.p.  $252^\circ C$  and a nitrosoderivative m.p.  $215^\circ C$  (decomp.) from the ethyl ester m.p.  $158^\circ C$ .

#### 175. Flavanes.

K. S. NARANG and J. N. RAY.

Chalcones on catalytic reduction are converted into dihydro derivatives which are transformed to flavanes analogous to catechin.

#### 176. Attempt to synthesise benzopyrillium salts.

M. GOSWAMI and A. K. CHAKRAVARTI.

Condensation of coumarin with resorcin with  $POCl_3$  gave a compound which from analytical results has been suspected to be a benzopyrillium salt and confirmation of the view is being made by preparing it from salicylic aldehyde and resacetophenone.

#### 177. The reaction of pyridene with 1 : 3 dichloro-4 : 6 dinitrobenzene.

H. S. JOIS and B. L. MANJUNATH, Bangalore.

When pyridene is warmed with 1 : 3 dichloro-4 : 6 dinitrobenzene vigorous reaction sets in with evolution of a small amount of hydrochloric acid. The resultant mixture was separated into two constituents. One of these, a colourless compound ( $C_{16}H_{12}O_4N_4Cl_2$ ), is highly soluble in water and the chlorine in it is quantitatively precipitated by aqueous silver nitrate. To this is assigned the dipyrindonium structure. It appears to melt at  $132^\circ$ , but changes over at that temperature to the second substance giving off HCl. This latter is a halogen free yellow compound (decomposes at  $180^\circ$ ) and its structure is being investigated.

#### 178. $\beta$ - $\beta$ Diaceto $\alpha$ $\gamma$ dibenzoyl propane.

A. U. QUERESHI and J. N. RAY.

The above substance and analogous bodies have been synthesised and converted into dihydro pyridines. Ketocyclol tautomerism of the above has been studied.

#### 179. Condensation of ethyl aceto-succinate and ethyl formylsuccinate with aromatic amines.

B. B. DEY and A. K. LAKSHMINARAYANAN.

The condensation has been effected by four different methods, viz., (a) interaction in the cold by leaving the mixture for a week in a desiccator over sulphuric acid, (b) rapidly heating the mixture to the boiling



point and maintaining at this temperature for a few minutes only (cf. Ewins and King, *J.C.S.*, 1913, 104), (c) mixing the components with excess of glacial acetic acid and boiling for several hours (cf. H. Liebermann, *Ann.*, 1914, 404, 272), and (d) mixing the components with a few drops of diethyl amine, leaving at the ordinary temperature for 2-3 days, and then heating to the boiling point for a few minutes (cf. Gibson, etc., *J.C.S.*, 1926, 2247). The following products have been isolated and analysed, and their properties studied. (1) aceto-succinic monanilide,  $\text{CH}_3\text{CO.CH. (CONHPh).CH}_2\text{COOEt}$ , m.p.  $90^\circ$ , (2) 2-hydroxy-4-methyl-quinoline-3, acetic acid, m.p.  $180^\circ$ , (3) anilino-aceto-succinic dianilide,  $\text{CH}_3\text{C(NH.Ph):C(CO.NH.Ph).CH}_2\text{CO.NH.Ph}$ , m.p.  $194^\circ$ , (4) p-toluidide of 2, 6-dimethyl-4, hydroxy- (or 4, 6-dimethyl-2, hydroxy-) quinoline-3, acetic acid, m.p.  $268^\circ$ , (5)  $\beta$ -anilido-itaconic acid diethyl ester,  $\text{Ph.NH.CH=C(COOEt).CH}_2\text{COOEt}$ , m.p.  $103^\circ$ , and (6)  $\beta$ -p-toluidino-itaconic acid diethyl ester,  $\text{CH}_3\text{C}_6\text{H}_4\text{.NH.CH=C(COOEt).CH}_2\text{COOEt}$ , m.p.  $110^\circ$ .

#### 180. 4-Methyl-quinoline- $\alpha$ -pyrone.

R. N. SEN and G. MUKHERJEE, Calcutta.

A substituent in the phenol molecule exerts a marked influence on coumarin formation by Pechmann's method (Cf. Clayton, *J.C.S.*, 1908, 2016). In order to study the influence of a hetero-ring attached to the phenol on coumarin formation, the condensation of 8-oxy-quinoline with acetoacetic ester has been investigated, and it is found that 8-oxy-quinoline like dimethyl-m-amino-phenol (*Ber.*, 1897, 30, 277) condenses with acetoacetic ester in absolute alcoholic solution in the presence of zinc chloride giving an  $\alpha$ -pyrone derivative in small yield. It dissolves both in mineral acids and hot caustic alkalies. It is peculiar that this quinoline- $\alpha$ -pyrone exists in two isomeric forms though it has not been possible to offer a plausible explanation for this isomerism.

#### 181. 2':4' Diacetoxy phenyl 2-methyl 6:7 methylenedioxy 8-methoxy 1:2:3:4 tetrahydro isoquinoline and its action on uterus excised or *in situ*.

B. D. KOCHHAR and J. N. RAY.

#### 182. Organo-metallic derivatives of quinoline and isoquinoline.

R. N. SEN and G. MUKHERJEE, Calcutta.

Quinoline and isoquinoline derivatives with antimony in the nucleus have now been prepared for the first time by Bart's reaction on 3-, 5-, 6-, 7-, 8-aminoquinolines and 5 (or 8)-amino-isoquinoline. It has been observed that the position of the amino group in the quinoline nucleus is of very great consequence: the 6- and 8-amino-quinolines yield only 10-15% of the stibinic acids, while 25-30% of the stibinic acids are obtained from 3-, 5-, and 7-amino-quinolines. The 2- and 4-amino-quinolines do not even respond to diazo reaction.

It has also been possible to obtain quinoline derivatives with a mercury atom in the nucleus by the action of mercuric acetate on 8-oxy-quinoline. The fact that 5-bromo-8-oxy-quinoline and 5:6-dibromo-8-oxy-quinoline are mercurated as easily as 8-oxy-quinoline shews that the mercury atom enters into the ortho position to the hydroxyl group.

The study of the therapeutic value of these organo-metallic derivatives of quinoline and iso-quinoline may lead to interesting results.



183. The reaction between phenylhydrazine and quinolinic acid.

A. C. SIRCAR and P. R. SEN GUPTA, Calcutta.

The action of phenylhydrazine with quinolinic acid has been studied and by taking different proportions of the reacting substances and using different temperatures, four different products have been obtained.

184. Anhydro-cotarnine derivatives.

G. S. AHLUWALIA, B. D. KOCHHAR, and J. N. RAY.

Cotarnine condenses with phenols in presence of sodium ethoxide. A number of these substances are described and a comparative study of their action on paramoecia is undertaken.

185. Antimalarials. Part II.

G. S. AHLUWALIA, B. D. KOCHHAR, and J. N. RAY.

A number of cotarnine derivatives have now been synthesised and their anti-malarial properties fully investigated.

186. Synthesis in the phenanthren sub group of iso-quinoline alkaloids.

K. S. NARANG, G. S. AHLUWALIA, and J. N. RAY.

O-nitroaldehydes have been condensed with isoquinolinium methohydroxides and by Pschorr transformation converted into phenanthren derivatives.

187. Studies in acridine derivatives.

R. N. SEN and S. ROY, Calcutta.

This investigation deals primarily with the preparation of various acridine derivatives by new methods with a view to study the effect of the nature and position of different auxochromic groups on the colour and fluorescence of acridine dyes.

The method of Meyer and Gross (*Ber*, 1899, 32, 2356) for the preparation of typical acridine dye, benzo-flavine, from *m*-toluylene diamine and benzaldehyde, involves three different operations; but it has been now found possible to obtain this dye in a single operation using sulphuric acid (d. 1.84) as the condensing agent at the temperature of the boiling water bath, the condensation of the aldehyde with the diamine and subsequent acridine ring formation with the elimination of  $\text{NH}_3$  and final oxidation all taking place simultaneously. Different aldehydes (e.g., dimethyl-*p*-amino-benzaldehyde, *o*- and *p*-nitro-benzaldehydes anisaldehyde, vanillin, furfuraldehyde, cinnamicaldehyde) have thus been successfully condensed with *m*-toluylene diamine to produce acridine dyes with different substituents in the 5-phenyl residue. It is interesting to note that pro-flavine base is also thus readily obtained from tetra-amino-diphenyl methane.

All known acridine dyes contain the amino group in the para position to the central C atom. Acridine dyes with the amino group in the *m*-position to the central C atom and therefore in the para position to the N atom have now been prepared for the first time by condensing tetramethyl-*p-p*-diamino-diphenyl-methane (reduction product of Bindschedler's green) with benzoic acid and *p*-nitro benzoic acid.

From a study of the different acridine derivatives it is concluded that



the acridine chromophore is really a very weak one and as such colours varying from yellow to deep orange can only be exhibited by acridine dyes.

It is remarkable that tetrazotised pro-flavine and benzoflavine couple with 'R' salt to form dyes substantive to cotton, producing red and bluish-red shades respectively.

188. Studies in heterocyclic compounds.

A. C. SIRCAR and S. C. SEN, Calcutta.

The reaction of o-amino-hydroxy group in 2-hydroxy-3-amino-phenazine has been studied and it has been found that unlike ortho-amino-phenol, the hydroxy amino phenazine is not so well adapted for the building of heterocyclic compounds. Evidently the already existing azine ring in the phenazine strongly militates against the otherwise easy reactivity of the orthoamino-hydroxy groups.

189. The influence of attached rings on the formation of heterocyclic compounds. Part I.

T. N. GHOSH, Bangalore.

It has already been shown (*Jour. Indian Chem. Soc.*, 1929, 6, 181) that o-phenylenedialkylthiocarbamides are easily converted into thioheptadiazine derivatives when treated with strong hydrochloric acid. In continuation of the same work, some new substituted dithiocarbamide derivatives of ethylene, naphthalene, phenanthrene have been prepared and subjected to the action of strong hydrochloric acid with the object of examining the effect of one or more benzene rings on their ease and nature of transformation into cyclic structures. From the results that have been obtained, it is concluded that the benzene ring helps the ring-formation and that the effect appears to increase with the increase in the number of benzene rings.

190. The influence of attached rings on the formation and stability of heterocyclic compounds. Part II.

T. N. GHOSH, Bangalore.

In order to confirm further the idea developed in Part I,  $\beta$ -amino-propionic acid has been condensed with various thiocarbimides to yield a mixture of a diazine and thiazine derivatives with the elimination of a molecule of water. It has already been shown (*Jour. Indian Chem. Soc.*, 1930, 7, 981) that the condensation of anthranilic acid with various thiocarbimides yields quinazoline derivatives. The evidence which has now been obtained from the action of hydrolysing agents on the above diazine and quinazoline derivatives points clearly to the well-marked influence of the benzene ring in increasing the stability of the heterocyclic systems. Similarly the velocity coefficients for the hydrolysis of succinimide, isatin etc., on one hand and phthalimide, naphthisatin on the other are being studied with a view to obtain further evidence in this connection.

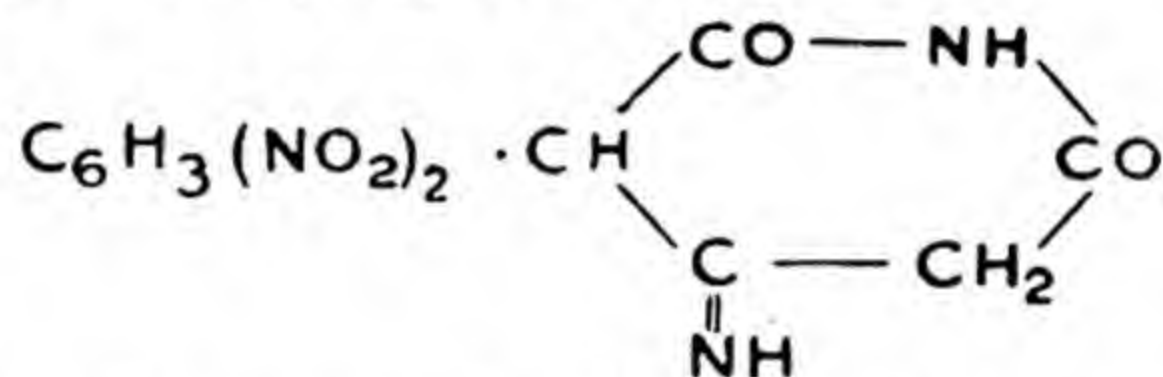
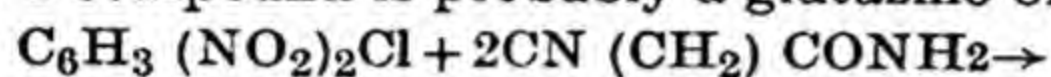
191. Interaction of dinitro-chlorobenzene with cyanoacetamide.

PULINBEHARI DAS and H. K. SEN, Calcutta.

Dey has found (Private communication) that when 1 mol. of 2,4-dinitro chlorobenzene is boiled with an alcoholic suspension of  $1\frac{1}{2}$  mol. of sodio-cyanacetamide for several hours a compound melting at  $188^{\circ}\text{C}$  after purification by crystallisation from acetic acid is obtained. It imparts an intense blue colouration with minutest quantities of alkali and gives even with ordinary distilled water a bluish tint, which disappears on acidifica-



tion. As such a behaviour appears unlikely from the ordinarily expected course of reaction the subject was investigated under different experimental conditions. For example, sodio-cyanacetamide prepared in absolute alcoholic suspension was washed thoroughly with ether and benzene and subsequently boiled under reflux for ten hours with 2-4-dinitrochlorobenzene in benzene suspension on the water bath. The separated product this time, after acidification, could be crystallised from boiling water with the help of animal charcoal when a very pale yellowish looking product of the composition  $C_6H_3(NO_2)_2CH(CN)CONH_2$  melting at  $166^\circ-168^\circ$ . On hydrolysis with 80 per cent. sulphuric acid, the dinitro-phenylacetic acid melting at  $188^\circ C$  was obtained establishing thus the constitution of the condensation product. It gives a red colouration with alkalis as distinct from the blue colour given by Dey's compound. On mixing equimolecular quantities of our compound and cyanoacetamide and boiling for some time the red colouration changes to blue but so far no pure compound has been isolated from the reaction product. The conjecture however is that Dey's compound is probably a glutazine of the following composition:—



On hydrolysis, the compound yielded a derivative insoluble in alkali melting at  $221^\circ C$  which is under investigation.

## 192. Endothio and endo-imino triazoles and thiobiazoles.

S. L. JANNIAH and P. C. GUHA, Bangalore.

The work reported in Science Congress abstract of 1931, No. 165, p. 47, has been extended further and several other isomeric endo-compounds in the triazole series have been isolated. 2 : 5-dithiol-1 : 3 : 4-thiobiazole on being treated with acetic anhydride gives an acetyl compound which on de-acetylation gives neither the original dithiolthiobiazole nor any isomeric endothio compound as expected from previous experience—but 2 : 2'-dithiol-dithiobiazole sulphide. Further work in this direction, by way of exploiting the possibility of formation of open chain, closed chain and bridged sulphides—is being continued with aliphatic and aromatic dithiol compounds.

## 193. Synthesis of phenylthioxanthenes.

GOPAL V. NEVGI and G. C. CHAKRAVARTI, Bangalore.

For the preparation of phenylthioxanthenes a more direct method, than the condensation of hydroxy benzhydrols with aromatic mercaptans (Betrabet and Chakravarti, *Proc. Indian Sc. Congress*, 1930) in presence of zinc chloride, was tried by condensing substituted diphenyl sulphides with aromatic aldehydes in presence of concentrated sulphuric acid. The products obtained were mostly the expected thioxanthenes and sometimes their sulphonic acid derivatives containing one or more sulphonic acid groups in the molecules. The yields were fairly good.

Phenylthioxanthenes were in this way obtained from the following sulphides, (1) p-methoxy-p'-methyldiphenyl sulphide, (2) m-methoxy-p'-methyldiphenyl sulphide, (3) p-methoxy phenyl  $\beta$ -naphthyl sulphide, (4) m-methoxy phenyl  $\beta$ -naphthyl sulphide, and the following aldehydes, (1) benzaldehyde, (2) p-nitro-benzaldehyde, (3) m-nitro-benzaldehyde, (4)



vanillin, (5) anisaldehyde, etc. The detailed investigation of the properties of the compounds obtained is being carried out. It is anticipated that the xanthenes derived from the m-methoxy compounds will on oxidation first yield the carbinol bases which on hydrolysis will then be converted into quinonoid derivatives.

#### 194. Organo arsenic compounds.

D. N. MAZUMDAR and P. C. GUHA, Bangalore.

The work already reported (*vide Science Congress Abstracts* 1930, p. 19, 1931, p. 40) has been extended further and a number of aromatic diamines like pp-diaminodiphenyl-urea, -oxamide, -malonamide, -succinamide, -carbohydrazide, -hydrazodicarbonamide, etc., have been arsenated by different methods.

#### 195. Preparation of mercury-organic compounds with the help of mercuric chloride and sodium bicarbonate in presence of glycerol. Part II.

P. NEOGI and M. M. GHOSE.

The method employed by Neogi and Chatterjee for mercuration of organic compounds has been extended to thymol, o-, m-, and p- toluidines, a- and b-naphthol and a- and b-naphthylamines.

#### 196. Vasicine.

K. S. NARANG, S. KRISHNA, T. P. GHOSH, and J. N. RAY.

New oxidation products and further degradative experiments throwing light on the constitution are now described.

#### 197. The alkaloids of kurchi bark (*Holarrhena antidysenterica*). Part II.

SUDHAMOY GHOSH and I. B. BOSE, Calcutta.

In a previous paper (Ghosh and Ghosh, *Jour. Ind. Chem. Soc.*, Vol. V, p. 477, 1928) it was shown that the kurchi bark contains, besides a little conessine, two new alkaloids designated by the authors as kurchine and kurchicine, the low-melting alkaloid, kurchine, occurring in largest amount. These two new alkaloids have now been further purified and properties of the bases and some of their derivatives have been studied. Kurchine, which has crystallised in colourless needles, is shown to have the composition  $C_{23}H_{38}N_2$ ; m.p.  $75^\circ$ ;  $[\alpha]_D^{32} + 6.4^\circ$  (in absolute alcohol),  $-7.57^\circ$  (in chloroform). The acid oxalate, which crystallises in colourless prisms, melts at  $221^\circ$  (whereas that of conessine melts at  $280^\circ$ ). The hydrochloride, hydrobromide, hydriodide, sulphate, platinic chloride have been crystallised and analysed.

The second alkaloid kurchicine, which crystallised in colourless needles, is shown to have the composition  $C_{20}H_{36}N_2O$ ; m.p.  $175^\circ$ ;  $[\alpha]_D^{32} - 11.44^\circ$  (in chloroform),  $-8.45^\circ$  (in absolute alcohol). The hydrochloride, hydrobromide, oxalate, sulphate, auric chloride and platinic chloride have all been analysed.

The results confirm that these alkaloids are different from conessine and holarrhenine isolated from the African holarrhena.



198. The chemical examination of the bark of *Moringa Pterygosperma*.

SUDHAMOY GHOSH and ASHUTOSH DUTT, Calcutta.

A preliminary extraction with solvents gave the following extractives : petroleum ether 0.71 per cent., sulphuric ether 6.47 per cent., chloroform 0.68 per cent. and absolute alcohol 2.17 per cent. The alcoholic extract gave strong reactions for alkaloids. An assay of the bark showed the presence of 0.105 per cent. of total vegetable bases. For isolation of the bases the bark was extracted by cold percolation with rectified spirit, the alcohol distilled off and finally concentrated in vacuo. The residue was extracted with dilute acid, filtered extract made alkaline and extracted with ether and finally with chloroform. The residue from the solvents was dissolved in alcohol, neutralised with HCl and evaporated. The dry residue was extracted with hot chloroform. The insoluble portion was repeatedly recrystallised from alcohol and the hydrochloride was obtained in colourless glittering plates, m.p.  $254.2^{\circ}$ . The platinic chloride crystallised in yellow rectangular plates of m.p.  $221^{\circ}$ , the picrate crystallised in yellow wooly needles m.p.  $195^{\circ}$ . The free base remained liquid at room temperature and could not be crystallised. The hydrochloride of the second base, soluble in hot chloroform, has not been obtained crystalline, but it had a strong physiological action.

## 199. Some new hydrocupreidine derivatives. Part II.

SUDHAMOY GHOSH and N. R. CHATTERJEE, Calcutta.

In a previous communication (*Jour. Ind. Chem. Soc.*, 1931, vol. 8, p. 257) we have described the preparation of some isoalkyl derivatives of hydrocupreidine. In the present paper the preparation of some of the normal alkyl derivatives of hydrocupreidine is described. They have been prepared, as before, by heating potassium hydrocupreidinate in absolute alcohol with the alkyl iodide using molecular copper as catalyst. The new bases, which crystallised well from acetone, were:—

- (1) Normal propyl hydrocupreidine  $C_{22}H_{30}O_2N_2$  (m.p.  $182^{\circ}$ )
- (2) Normal butyl hydrocupreidine  $C_{23}H_{32}O_2N_2$  (m.p.  $176^{\circ}$ )
- (3) Normal amyl hydrocupreidine  $C_{24}H_{34}O_2N_2$  (m.p.  $164^{\circ}$ )
- (4) Normal heptyl hydrocupreidine  $C_{26}H_{38}O_2N_2$  (m.p.  $158^{\circ}$ )
- (5) Normal octyl hydrocupreidine  $C_{27}H_{40}O_2N_2$  (m.p.  $151^{\circ}$ )

The antiseptic and other properties of iso-alkyl derivatives are still being studied. The use of any of these derivatives as local anaesthetic, bactericide or antiseptic would help to utilise the starting material, hydroquinidine, a normal constituent of the cinchona bark, now without any use.

200. Chemical examination of the roots of *Aristolochia Indica* (Linn.).

B. L. MANJUNATH, Bangalore.

The roots of *Aristolochia Indica* enjoy considerable reputation in Ayurvedic medicine as remedy for snake-bites, etc. A tincture is also used as a bitter tonic. Mention is made in the literature of the occurrence of a volatile oil and of an alkaloidal constituent.

The paper presents the results of a systematic study of the chemical constituents.



Successive extraction with the following solvents				Per cent. of extract.
Petroleum ether (b.p. 40—50°)	..	..	..	2.7
Ethyl ether	..	..	..	0.9
Chloroform	..	..	..	1.0
Ethyl acetate	..	..	..	0.5
Ethyl alcohol	..	..	..	5.1
				<hr/>
Total ..				10.2
				<hr/>
Essential oil content ..	..	..	..	0.46

An aqueous extract of the roots gave tests for the presence of starch and a small amount of reducing sugars. No tannin material could be detected.

The alkaloidal content was found to vary very greatly in different samples. An ether soluble base has been obtained in a pure state and its derivatives studied.

## 201. Oil from the fruits of *Solanum Xanthocarpum*.

SHANTI SHETH and D. D. KANGA.

The drug belongs to the Natural Order Solanaceae.

The oil was obtained by extracting the powdered fruits with petroleum ether in a Soxhlet apparatus.

It gives the following analytical data:—

Sp. Gr. at 15°C	..	..	..	0.9663
Refractive index at 40°C	..	..	..	1.4695
Iodine value	..	..	..	122.08
Saponification value	..	..	..	184.1
Reichert Meissl value	..	..	..	00.0
Acid value	..	..	..	64.75

Further work on the oil is in progress.

## 202. Oil from the seeds of *Celastrus peniculatus*.

SHANTI SHETH and D. D. KANGA.

The drug belongs to the Natural Order Celastrineae.

The oil was obtained by extracting the powdered seeds with petroleum ether in a Soxhlet apparatus. The yield of the oil was found to be 35 to 40 per cent. It is reddish brown in colour, bitter in taste and having a characteristic odour of its own. The oil was also obtained by pressing in the country Ghani. Table I. includes analytical data obtained by Solanki, Nargund and Kanga and the authors.



TABLE I.

	SHETH AND KANGA.		SOLANKI, NARGUND AND KANGA.*
	Pet. Ether extracted oil.	Ghani oil.	Pet. Ether extracted oil.
Sp. Gr. at 15°C ..	0.9670	0.9705	0.9566
Refractive index $n_D$ at 40°C ..	1.4701	1.4591	1.4547
Acid value ..	23.11	27.97	29.57
Iodine value ..	105.6	50.5	103.01
Saponification value ..	236.3	239.2	205.82
Reichert Meissl value ..	33.63	14.76	26.64
Unsaponifiable matter ..	.....	.....	8.355
Yield of the oil ..	35—40%	.....	40—45%

\* Proc. Ind. Sc. Congress, 1928.

Table II. gives constants for the mixed fatty acids.

TABLE II.

	Pot. Ether extracted oil.	Ghani oil.
Neutralisation value ..	124.68	169.6
Mol. weight (M.W.) ..	320.8	235.8
Iodine value ..	352.5	50.6
Titre test ..	36.6°C	22.0°C
Refractive Index $n_D$ at 40 C ..	1.4607	1.4473

Table III. gives constants for the saturated and unsaturated acids obtained from the mixed fatty acids from Ghani oil.

TABLE III.

	Saturated acids.	Unsaturated acids.
Molecular weight ..	252.04	280.7
Iodine value ..	1.95	77.2
Titre test ..	46.0°C	.....
Refractive Index $n_D$ ..	1.4328 at 60°C	1.4479 at 40°C

Further work on the oil is in progress.



203. Oil from *Hibiscus cannabini* seeds.

S. Y. KOLHATKAR.

The following are the constants of the oil which is contained to the extent of 18.10 per cent. in the seeds.

Sp. gr. 0.9232; refractive index: 1.45916; acid value: 0.89; iodine value: 98.73; saponification value: 199.1; R.P. value: 0.20; Polenski value: 0.05; unsaponifiable matter: 1.04; acetyl value: 19.2; unsaturated acids: 76.66 per cent.; saturated acids: 23.34 per cent.

204. Oil from *Tribulus Terristris* fruits.

S. Y. KOLHATKAR.

The following are the constants of the oil.

Sp. gr.: 0.9241; refractive index: 1.46428; acid value: 1.32; iodine value: 141.05 (semi-drying oil); saponification value: 206.25; R.P. value: 0.25; Polenski value: 0.09; unsaponifiable matter: 1.2623 per cent.; acetyl value: 16.01; unsaturated acids: 86.60 per cent.; saturated acids: 12.40 per cent.

205. Investigations on the seeds of *Carica-papaya*.

N. DESIKACHAR and V. SAMPAT IYENGAR, Bangalore.

The seeds of *Carica-papaya* are used in medicine for various purposes. The present investigation forms a systematic chemical and biochemical analyses of the whole seed.

Successive extraction with the following solvents gave:—

Petroleum ether (40–50 B.P.)	= 32.6 %
Chloroform	= 0.52 %
Alcohol	= 0.86 %

The petroleum ether extract gave a light yellowish green coloured oil which has the following constants:—

Sp. gravity (25°C.)	= 0.88
Refractive index (25°C.)	= 1.458
Iodine value (Hubles)	= 304.0
Saponification value (1 hr.)	= 234.7
Free acids	= 2.86

Detailed investigations are being carried out on the oil. The alcoholic extract gave tests for reducing and non-reducing sugars. Starch was absent in the alcohol extracted residue.

The seeds were further tested for the presence of different enzymes. The presence of amylase and lipase was distinctly shown, while traces of oxidase, peroxidase and catalase appeared to be present.

Further investigations on the presence of the above enzymes and proteases in germinated seeds are in hand.

## 206. Calamus.

N. C. KELKAR and B. SANJIVA RAO, Bangalore.

The oil obtained by distillation of the Indian root contains asarone (81 per cent.) terpenes (0.5 per cent.).

## 207. Study of tar from Cashew nut.

Y. K. RAGHUNATHA RAO.

The properties of tar from Cashew nut (*Anacardium Occidentale*) have been studied. The tar yields 35 per cent. distillate, a light yellow oil (B.P. 200–300°C at atmospheric pressure) and density 0.89 at 25°C.



Condensations of the distillate and of the tar with formaldehyde, acids, alkalies and oxidizing agents give light coloured or dark resins suitable for quick drying varnishes, impregnations and mouldings.

208. Studies in fish oils, Part I—Investigation of the factors involved in the technical preparation and storage of medicinal cod liver oil with respect to its vitamin potency.

K. D. GUHA, Bangalore.

Different batches of selected livers were 'cooked' in a small boiler (practically designed on the model of those used in the industry itself) with direct steam under different pressure to prepare the oil and the quality of the samples studied in relation to the conditions of livers, steam pressure, storage, refining, etc. An attempt has also been made to define the dietetic standard of cod-liver and certain other fish-liver oils.

209. The growth promoting factors in Indian dairy products.

N. C. DATTA and B. N. BANERJEE, Bangalore.

Very little is known regarding the growth promoting factors of Indian cow milk and its different products. Feeding experiment with Albino rats were used in determining the growth promoting factor.

The milk of a Scindi cow (yielding 17 lbs. of milk daily) kept at the Imperial Institute of Dairy and Animal Husbandry were used. The cow was on standard ration throughout the experiment. Butter and ghee were prepared from the milk of the same sample. By studying the growth of Albino rats with fresh milk and its products as a supplement to the basal diet, it was found that fresh milk was the best source of growth promoting factor. Milk sterilized at (15 lbs. for 15 mins.) suffered slight loss of this factor. The potency of butter and remelted butter were much less—nearly half that of fresh milk. Remelted butter (ghee) was found to be as good as butter.

The effect of cold storage on butter and ghee and further work on this line is in hand.

210. Stick-lacs: their composition and physical properties.

M. VENUGOPALAN and S. RANGANATHAN.

Stick-lacs of known origin have been collected from various parts of India, cleaned under the same conditions and the washed products analysed into wax, ether-soluble resin and alcohol-soluble resin. Softening and melting points, acid and iodine values were determined. Thin films prepared from these lacs have been tested for abrasion resistance and scratch hardness. On the strength of the above data certain tentative conclusions have been drawn as to their specific characteristics, in composition and physical properties, with a view to their classification on scientific lines.

211. Examination of some Calcutta pulses.

N. C. NAG and H. N. BANERJEE.

In a previous communication published in the Proc. XVIth Indian Science Congress, composition of some common pulses was dealt with. That work has been further extended. In addition, the oils have been analysed, and different constituents determined. The usual constants such as iodine value, saponification number etc., have been dealt with. Of particular interest have been the absorption photo-spectrographs (visible range about 7,200 to 4,000 Å. units) obtained in various solvents. Carotinoid pigments have been detected particularly in the unsaponi-



fiable portion of the oils. Their connection with vitamins are being examined. Fuller details will be published later on. An abstract of results of chemical analysis in one particular case, viz., *Cicer arietinum*—chhola, is given below :—

Percentage of oil—4.2% ; Iodine value—130 (Hanus method)

Fatty acids in oil—90% ; Iodine value—140

Unsaponifiable matter in oil—1.5%, identified as "Phytosterol, melting point 137°C.

Unsaturated liquid acid (Twitchel)—90% ; Iodine value—145 (Hanus)

Solid acid " —10% ; Iodine value—30 "

Separation of the constituents in the liquid unsaturated acid mixture was effected by preparing their bromo-derivatives and identified by estimation of bromine content as also the melting points of the derivatives.

Oleic acid—38.41% ; Linolic acid—59.36% ; Linolenic acid—2.23%.

## 212. The Chemistry of some west coast fish oils.

P. RAMASWAMI AYYAR, Bangalore.

A preliminary study of Mangalore 'Sardine' oil has been made and similar work on Embryonic 'Dog-Fish' liver oil and 'Shark' liver oil from Vaikom is in progress.

## 213. Sweating of soaps.

M. GOSWAMI and K. L. BOSE.

Anhydrous and hydrated soaps of lauric, myristic, palmitic, stearic and oleic acids have been examined individually and severally in proportions in which they are approximately present in commercial soap, as regards the absorption of moisture under standard conditions with and without inhibiting reagents.

## 214. Electrometric determination of the acid value and saponification value of resins.

N. NARASIMHA MURTY.

A potentiometric method involving the use of quinhydrone electrode has been evolved for the determination of the acid value and saponification value of resins. 95 per cent. alcohol is used as the solvent ; and, for reference electrode, a saturated solution of lithium chloride in 95 per cent. alcohol with quinhydrone electrode is used. The acid value and saponification value of shellac, seed lac, wax-free lac, bleached lac, ether-soluble lac, ether-insoluble lac, rosin, pontinac, and sandarac have been determined by the new method. Standardisation of the alcoholic potash with alcoholic solution of benzoic acid is recommended instead of with the aqueous solution which gives higher value for the normality. On account of the obvious advantage which the quinhydrone electrode has over the hydrogen electrode, the method can be adopted in all industrial laboratories for the determination of acid value and saponification value of resins.

## 215. Studies in fish oils. Part II—A comparative study of the chemical composition of different kinds of marine and fresh-water fish oils in relation to their medicinal value.

K. D. GUHA, Bangalore.

A quantitative method has been developed to determine percentage composition of the most complex mixture of fatty acids occurring in



fish oils. The liver oils of cod, hake, dog-fish etc., and the body oil of the Indian sardine together with that of the sweet-water fishes, namely, ruhit, dhain, hilish, mrigel, etc., from Bengal have been investigated.

216. Investigation of the oil of *Clupea ilsha*.

M. GOSWAMI and JAGADANANDA DATTA.

The oil was rendered very easily from the fish which is abundantly found in Bengal and detailed examinations as regards the qualitative and quantitative values, constituents and Hilditch's ratio, etc., have been done.

217. Estimation of  $\psi$ -morphine in commercial morphine.

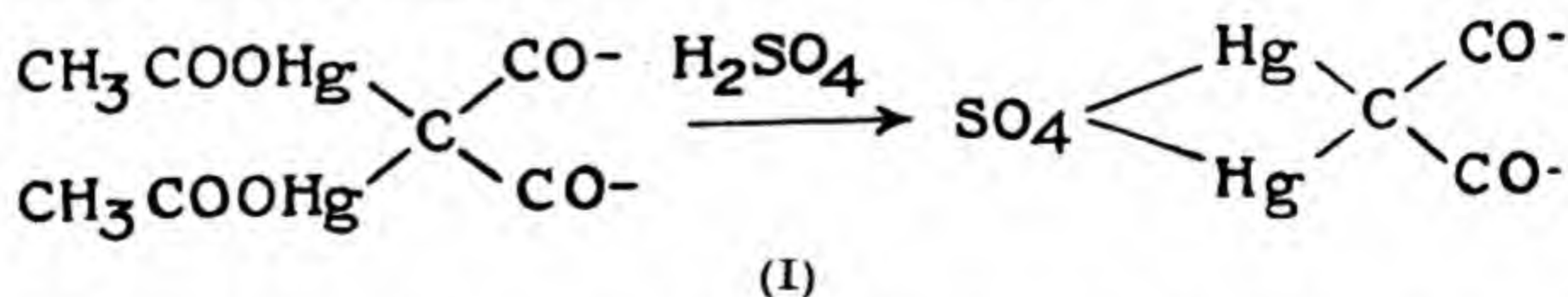
G. S. AHLUWALIA and J. N. RAY.

A quantitative method has been worked out for the above estimation based, on the insolubility of morphine sulphate in dilute alcohol.

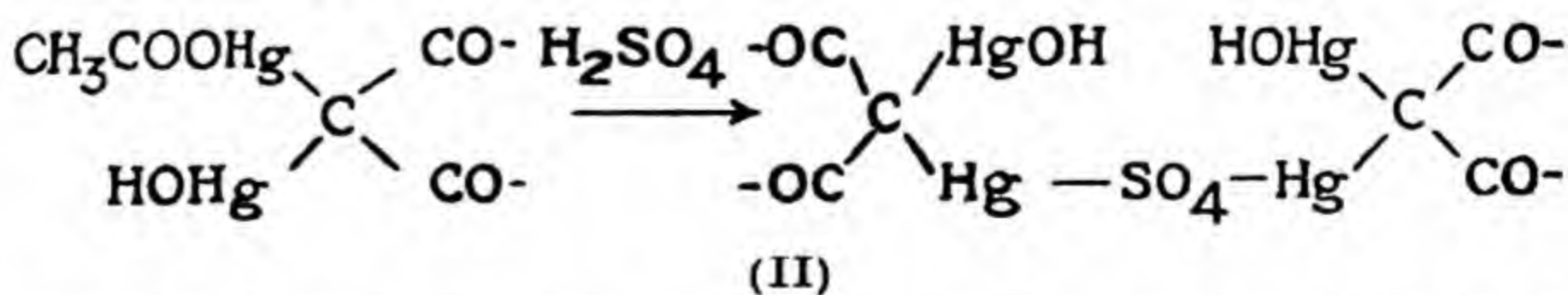
218. Mercuration of compounds containing a reactive methylene ( $-\text{CH}_2-$ ) group.

K. G. NAIK and R. P. PATEL, Baroda.

Mercuric acetate was employed to mercurate the following substances:—(1) acetoacetanilide, (2) acetoacet-o-toluidide, (3) acetoacet-p-toluidide, (4) acetoacet-m-toluidide, (5) acetoacet- $\alpha$ -naphthylamide, (6) acetoacet- $\beta$ -naphthylamide, (7) acetoacet-1:3:4-xylidide, (8) acetoacet-1:4:5-xylidide, (9) acetoacetic ester, (10) acetoacet-m-nitranilide, (11) ethyl malonate, (12) malon-mono-phenylamide, (13) malon mono-o-toluidide, (14) malon mono-p-toluidide, (15) malon mono-m-toluidide, (16) malon mono- $\alpha$ -naphthylamide, (17) malon mono- $\beta$ -naphthylamide, (18) malon mono-1:3:4-xylidide, (19) malon mono-1:4:5-xylidide and (20) malonamide. Compounds of the following two types were obtained. Whereas compounds 1-11 reacted with mercuric acetate in methyl alcohol giving diacetoxy-mercury derivatives of the formula (I)



compounds 12 to 20 reacted under similar conditions giving compounds of the constitution (II):—



Compounds of type I gave sulphatomercury derivatives; while those of the type II gave hydroxysulphatomercury derivatives as shown above. Action of potassium iodide and sodium hydroxide supported the above constitution. From the action of dilute hydrochloric acid, hydrogen sulphide and potassium iodide, it appears that the linkage between the

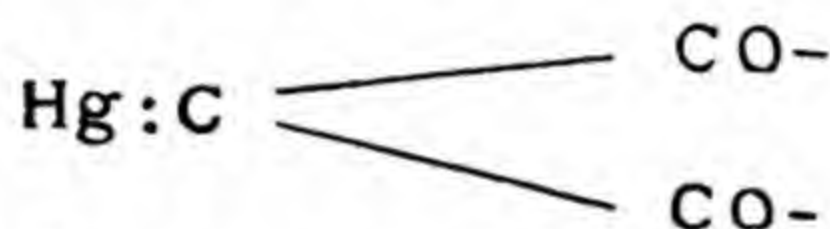


carbon atom of the reactive methylene group and mercury, is a very weak one as is expected from compounds containing a mercury attached to a carbon atom in a position alpha to a carbonyl group.

219. Interaction of mercuric chloride with substances containing a reactive methylene group.

K. G. NAIK and R. P. PATEL, Baroda.

In previous work (*J.I.C.S.*, 1930, 7, 655) it was shown that equimolecular quantities of mercuric chloride and sodium bicarbonate react in the cold with compounds containing a reactive methylene group, giving dichloro derivatives. However, during the course of the reaction described here, sodium bicarbonate was taken in excess and the mixture heated, expecting that the hydrolysis would proceed to completion and the nascent mercuric oxide formed during the course of reaction, would react giving compounds with C: Hg linkage. The action of mercuric chloride has been studied with the following substances:—(1) malon monophenylamide, (2) malon mono-o-toluidide, (3) malon mono-m-toluidide, (4) malon mono-p-toluidide, (5) malon mono- $\alpha$ -naphthylamide, (6) malon mono- $\beta$ -naphthylamide, (7) malon mono-1:3:4-xylidide, (8) malonamide, (9) ethylacetoacetate, (10) acetoacetanilide, (11) acetoacet-p-toluidide, (12) acetoacet-o-toluidide, (13) ethyl malonate. Compounds of the following constitution were obtained:—



These compounds decomposed on treatment with dilute hydrochloric acid, hydrogen sulphide, potassium iodide and phenyl-hydrazine. These reactions indicate a weak carbon-mercury linkage as is always found, when the mercury atom is attached to a carbon atom, in a position alpha to a carbonyl group.

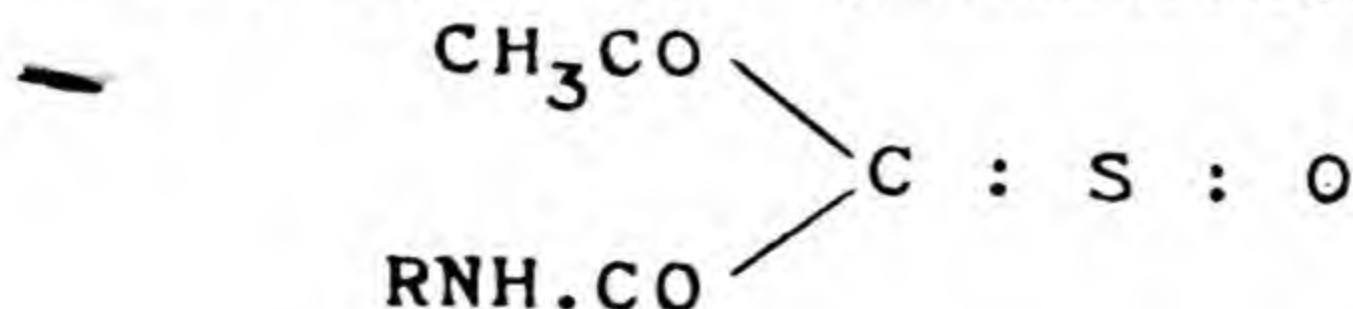
220. Interaction of thionyl chloride in *boiling benzene* with substances containing a reactive methylene ( $-\text{CH}_2-$ ) group.

K. G. NAIK and V. B. THOSAR, Baroda.

In continuation of previous work (*J.I.C.S.*, 1930, 7, 137, 145) the action of thionyl chloride in *boiling benzene* was further studied with the following compounds.

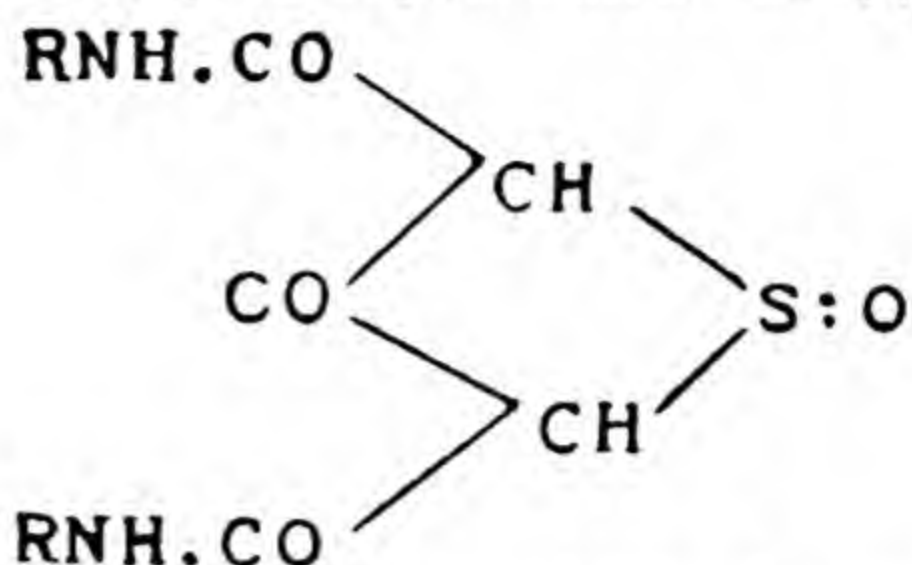
(1) Acetoacet-anilide, (2) acetoacet-o-toluidide, (3) acetoacet-m-toluidide, (4) acetoacet-p-toluidide, (5) acetoacet- $\alpha$ -naphthyl amide, (6) acetoacet- $\beta$ -naphthyl amide, (7) acetoacet-xylidide (1:3:4), (8) acetoacet-xylidide (1:4:5), (9) acetone-dicarboxy-anilide, (10) acetone-dicarboxy-o-toluidide, (11) acetone-dicarboxy-p-toluidide, (12) acetone-dicarboxy- $\alpha$ -naphthyl amide, (13) acetone-dicarboxy- $\beta$ -naphthyl amide.

Amides (1) to (8) gave rise to sulfoxides of the general constitution,





whereas amides (9) to (13) gave sulfoxides of the type



As compared with the sulfoxides obtained from substituted amides of malonic acid these were stable in boiling benzene with excess of thionyl chloride or dry hydrochloric acid gas and towards moisture, in as much as they were neither degraded into sulphides nor decomposed by such treatment.

The results of the present investigations afford a clear evidence that the reactivity of thionyl chloride with compounds containing a reactive methylene ( $-\text{CH}_2-$ ) group depends largely upon the electronegative character of the attached grouping.

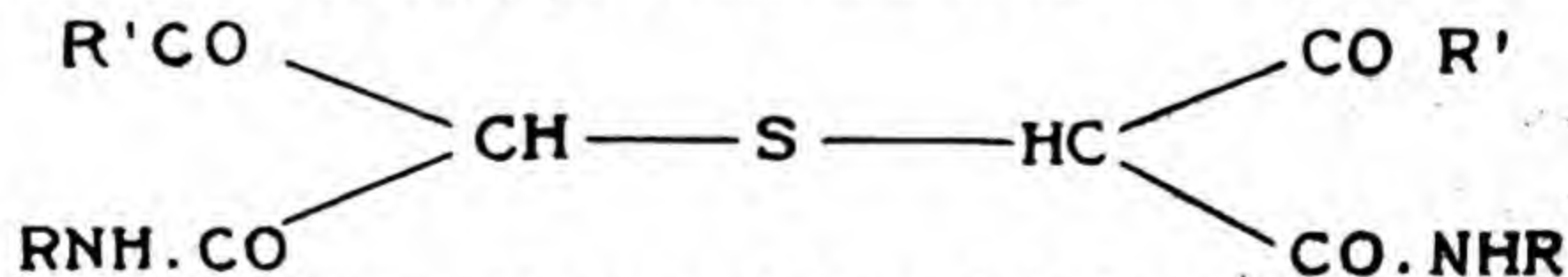
## 221. Interaction of thionyl chloride in the *cold* with substances containing a reactive methylene ( $-\text{CH}_2-$ ) group.

K. G. NAIK and V. B. THOSAR, Baroda.

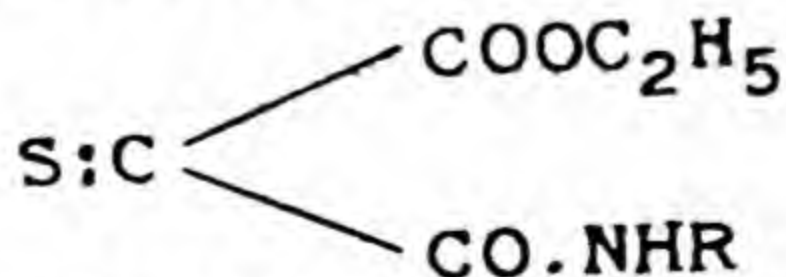
From literature it is evident that the course of reaction followed by thionyl chloride is entirely guided by the conditions of the experiments. Hence it was thought interesting to examine the course of reaction followed by thionyl chloride when it reacts with substances containing a reactive methylene ( $-\text{CH}_2-$ ) group in *cold ethereal solution*, although a similar reaction in *boiling benzene solution* had resulted in the formation of sulfoxides. The following compounds were investigated.

(1) Acetoacet-anilide, (2) acetoacet-o-toluidide, (3) acetoacet-m-toluidide, (4) acetoacet-p-toluidide, (5) acetoacet- $\beta$ -naphthyl amide, (6) acetoacet-xylidide (1 : 3 : 4), (7) malon-di-n-propyl amide, (8) malon-di-isobutyl amide, (9) ethylmalon-o-tolyl amate, (10) ethylmalon-p-tolyl amate, (11) ethylmalon- $\beta$ -naphthyl amate, (12) ethylmalon-xylil amate (1 : 3 : 4), (13) ethylmalon-xylil amate (1 : 4 : 5).

Compounds (1) to (8) gave compounds of the constitution,



while the amates (9) to (13) gave sulphides of the formula



All these compounds are white crystalline products, quite analogous in properties to the sulphide of acetoncetic ester described by Michaelis and Philips (*Ber.*, 23, 559).



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## ABSTRACTS OF PAPERS.

### Section of Geology.

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CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Geology.

### *Abstracts.*

### **MINERALOGY.**

1. On the mode of occurrence and origin of Cummingtonite in the limestones of the Kudurekanive Range of Hills, Tumkur District (Mysore State).

B. BALAJI RAO *and* B. RAMA RAO, Bangalore.

The clove brown mineral conspicuously occurring in some of the limestone outcrops of the Kudurekanive range of hills, near Huliya (13° 35' : 76° 33'), has been indentified by its physical and optical characters and by its chemical composition to be a variety of Cummingtonite. The presence of a ferruginous amphibole as a secondary mineral in a highly calciferous limestone being unusual, its mode of occurrence was studied in the field and this has disclosed that the mineral has been formed as a result of metamorphism in the portions of the limestone where it is interlaced with bands of ferruginous quartz schist. It is evident that the requisite amounts of iron and silica for the crystallisation of Cummingtonite in the limestone matrix, have been contributed by the ferruginous quartz schist. The question whether the latter rock has found its place in the limestone as a set of intrusive veins or as veins of replacement by circulating solutions has been briefly touched upon. Though the evidence is neither definite nor conclusive, yet it seems to indicate the probable igneous mode of origin of the ferruginous veins.

2. A note on the constitution of Cummingtonite.

E. R. TIRUMALACHAR *and* M. B. RAMACHANDRA RAO, Bangalore.

A study of the chemical analyses of Cummingtonite from several localities has shown that there is an excess of silica over the metasilicate ratio in each case. In many of the samples there is water, sometimes running up to as high as 3 per cent. and it is shown that this water is not likely to be constitutional but only held in solid solution. The constitution of Cummingtonite is then explained as a mixture of ortho- and poly-silicates of iron and magnesium, and the differences in the proportions of FeO and MgO explain the apparent excess of silica over the metasilicate ratio.

3. On the zoned feldspars from the Porphyries near Mysore.

S. R. NARAYANA RAO *and* B. S. BHIMA RAO, Bangalore.

The paper records certain observations made regarding the exact nature and constitution of the zonary banding noticed in some of the feldspar phenocrysts from the porphyries near Mysore. Attention is drawn to the variations in the composition of the different zones—as indicated by micro-chemical methods. Some peculiarities relating to the mode of alteration of these zoned feldspars are pointed out and their significance discussed.



## 4. A study in the uralitisation of Hornblende.

K. SRIPADA RAO and M. B. RAMACHANDRA RAO,  
Bangalore.

While the nature of the uralitisation of pyroxenes is fairly well known, there has been little or no information regarding the transformation of amphiboles into Uralite. The present paper serves to throw some light on this problem and is a study in the uralitisation of Hornblende—from an amphibolite found near Sakarsanhalli ( $12^{\circ} 47' : 78^{\circ} 13'$ ), Kolar District. From a detailed study of the Uralite in relation to the Hornblende and comparison with the similar alteration product known to be associated with pyroxenes, it is shown that the probable causes for, and processes involved in, this type of mineral alteration are essentially similar in the two cases.

5. Ilmenite crystals from Kishengarh State ( $26\frac{1}{2}^{\circ} : 75^{\circ}$ ),  
Rajputana.

S. L. BISWAS and B. MAITRA, Calcutta.

The crystals show distinct cleavage parallel to the basal pinacoid. Forms developed are  $c$ ,  $s$ ,  $r$ ,  $n$ ,  $a$ ,  $e$ ,  $n_1$ ,  $\zeta$ ,  $m$ , (Dana) and also the new forms  $\zeta_1$  ( $2\bar{2}05$ ),  $q$  ( $05\bar{5}4$ ), and  $\rho$  ( $40\bar{4}5$ ).

A stereographic projection of the different forms is given.

6. A short note on the habit and the alteration of  
Magnetite.

S. LAKSHMANA RAO, Bangalore.

The mineral described in the paper is found in the highly altered ultrabasic rock, near Talur Chrome Mines ( $12^{\circ} 11' : 76^{\circ} 37'$ ), Mysore District. It is isometric in crystal system and occurs in cubes and combination of cubes and octahedrons. The development of new faces due to corruptions has been just noted. Spinel type of twinning as well as oscillatory combinations, the latter, in microsections, have been noticed. The mineral has dark brown colour, submetallic lustre with a brownish tarnish, and reddish brown streak. Its hardness is 5–5.5 and Sp. Gr. 4.23. Its chemical composition is  $\text{Fe}_2\text{O}_3$  84.83%;  $\text{Cr}_2\text{O}_3$  0.48%;  $\text{SiO}_2$  4.15%;  $\text{Al}_2\text{O}_3$  0.10% and  $\text{MgO}$  in traces,  $\text{H}_2\text{O}$  7.92% and its formula is  $5 \text{Fe}_2\text{O}_3 \cdot 4 \text{H}_2\text{O}$ . Its habit and its angular measurements show the mineral to be magnetite, but its chemical composition, streak and low specific gravity and non-magnetic property confirm the mineral to be a pseudomorph of hydrous ferric oxide having the formula  $5 \text{Fe}_2\text{O}_3 \cdot 4 \text{H}_2\text{O}$ .

7. On the secondary pyroxenes and associated minerals  
from the Tarurites of the Sakarsanhalli Area, Kolar  
District (Mysore State).K. SRIPADA RAO and M. B. RAMACHANDRA RAO,  
Bangalore.

The paper deals with a detailed study of the Tarurites from the Sakarsanhalli area ( $12^{\circ} 47' : 78^{\circ} 13'$ ), Kolar District, especially with a view to investigating the nature of the secondary pyroxenes and associated minerals contained therein. On the basis of their optical characters and chemical constitution, it has been shown that the so-called 'Secondary Augites' of this rock are really of the nature of Diopside.



Attention is drawn to the occurrence, associated with these secondary pyroxenes, of Rhodonite, Spessartite and Scapolite, and the interesting question of the exact mode of origin of these minerals in this area is next discussed. Apart from these, a few minerals allied to Blanfordite and Piedmontite are tentatively identified in some of the sections.

#### 8. An alternative formula for the mineral Vredenburgite.

M. R. ANANTANARAYANA IYER, Bangalore.

In view of the fact that Vredenburgite is strongly magnetic and that other strongly magnetic minerals belong mostly to the spinel group, the analytical figures for the two specimens of the mineral given in Dr. Fermor's Manganese Memoir are recast so as to give a spinel grouping in the formula. The formula suggested for the mineral is a combination of the formula for the mineral Bixbyite and of the formula for the spinel group of minerals. The results of analyses of three more samples of the mineral are given and it is shown that the same type of formula could be given for all these. The composition of one of the specimens is noteworthy because the spinel portion also of its formula contains iron and manganese in equal proportion. It is suggested that Sitaparite, another manganese mineral, may be classed under this group as a distinct species.

### ORES.

#### 9. Chromite deposits in Mysore.

T. P. KRISHNACHAR, Bangalore.

In Mysore, chromite deposits are practically confined to ultrabasic members of Dharwar system. Lens-shaped ore-bodies in Hassan District lie along Nuggihalli schist-belt ( $13^{\circ} 1'$ :  $76^{\circ} 28'$ ), in talc-serpentine matrix, while near Mysore chromite veins occur in altered dunite rocks. These ultrabasic rocks are intrusive into original hornblende-schist and are intruded by later gneisses.

Surface and underground observations do not favour the suggestions made regarding the altered dunite rock being a peridotite member in the basic division of charnockites.

Serpentine and Magnesite have been formed by the alteration of Olivine (in Mysore District) and Enstatite (in Hassan District) through the agency of water charged with carbon dioxide.

From the cooling ultrabasic magma, Chromite was separated out as the first basic differentiate and the degree of concentration (i.e., segregation) varies from the pure aggregate of a lens to the ultrabasic rock with some grains of Chromite.

High-grade ore deposits of Hassan District are being worked by open quarrying, and those near Mysore by underground methods. Near Arsikere ( $13^{\circ} 19'$ :  $76^{\circ} 15'$ ) a concentration plant is now set up to concentrate the low-grade ores. Some experiments are being conducted by the Mysore Government to produce ferrochrome from the high-grade ores of the state.

#### 10. Microscopic characters of Bawdwin Ores.

S. K. ROY and S. KRISHNASWAMY, Dhanbad.

The authors made a systematic study of the polished specimens of Bawdwin ( $23^{\circ} 7'$ :  $97^{\circ} 19'$ ) ores collected by one of them and during their investigations discovered Tetrahedrite, Bornite, Proustite, Pyrrhotite, etc., not reported from this area before.



This paper also includes a hitherto unpublished detailed geological map of the mining area on the scale 1"=400 ft. The authors have reclassified the Bawdwin volcanic series into

- (i) Bawdwin tuffs
- (ii) Teddy grits
- (iii) Chloritoid schist
- (iv) Rhyolites

and described their micro-characters fully.

Incidentally, this is the first instance of microscopic examination of polished ores carried out in India.

# 11. Note on the kaolin deposit of Manjhapara (Gangpur State, Bihar and Orissa).

D. P. CHANDOKE, Calcutta.

Kaolin is derived by the alteration of a pegmatitic boss, intrusive into Dharwar phyllites at Manjhapara ( $22^{\circ} 2' : 84^{\circ} 12'$ ). The pegmatite possesses large weathered zones of Felspar, with occasional segregations of Rubellite, and a black variety of Tourmaline.

Kaolin is especially rich in alumina, and the percentages of iron and moisture are low. The results of analysis are compared with those for consignments received in India from Cornwall, and also those prepared at the Kasimbazar Mines. The Manjhapara product possesses low plasticity and crumbles away at  $1400^{\circ}\text{C.}$ , without showing any colouration. The deposit is about  $1\frac{1}{2}$ —2 furlongs long.

## IGNEOUS ROCKS.

# 12. A preliminary note on Khanapur Gneiss.

K. V. KELKAR, Poona.

A massive granitoid type of gneiss occurs around Khanapur ( $15^{\circ} 38' : 74^{\circ} 31'$ ), Dt. Belgaum (Bombay). It consists of Orthoclase, Quartz, Biotite, and a subordinate amount of Oligoclase, Microcline and Muscovite. Porphyroblasts of Felspar, chiefly Orthoclase, are embedded in a matrix of granular Felspar and Quartz and Mica flakes. The gneissic structure is usually well developed. In thin sections are observed Apatite, Zircon, Magnetic iron ore, Epidote, Zoisite and granules of Sphene. The gneiss exhibits resemblances to the Bundelkhand type of gneisses.

# 13. Geology of Pallavaram Hill: the type area of the Charnockite series.

T. N. MUTHUSWAMY and C. MAHADEVAN, Madras.

The type area of Charnockite series, i.e., Pallavaram Hill ( $13^{\circ} 0' : 80^{\circ} 12'$ ), was geologically mapped in detail (Scale 1"=250 ft.). Besides noting the contact relations and transitions in the members of the series from leptynites to acid, intermediate and basic varieties, a special study of the basic veins and dykes was also made. Petrological examination of over eighty field specimens representing the gradations discloses various stages of differentiation of the original magma. Structural and paramorphic changes in the minerals as observed under the microscope are also described and discussed in relation to the geological history of the area.



14. Dolerite dykes of the western parts of the Raichur Do-ab (Hyderabad State).

H. S. KRISHNA MURTHY, Hyderabad State.

The Dharwar schists and the Peninsular gneisses in the Raichur Do-ab ( $16^{\circ} : 77^{\circ}$ ), are cut by a number of dolerite dykes, which intersect one another frequently and evidently are not of the same age. The paper discusses their distribution, structural features, relative age, and contact relations with the country rocks. The paper is illustrated by maps and micro-sections.

15. A short note on Sylhet Trap.

P. C. DATTA, Calcutta.

This short note embodies the results obtained from a chemical and physical study of the rocks collected from the neighbourhood of Cherra Punji ( $25^{\circ} 17' : 91^{\circ} 44'$ ), Khasi and Jaintia Hills (Assam).

16. On the nature of the spots found in the trap rocks near Lingadahalli, Kadur District (Mysore State).

CHARLES S. PICHAMUTHU, Bangalore.

There has been some difference of opinion on the question of the exact nature and mode of origin of the ovoid and irregular spots and patches frequently noticed in the Trap rocks of the Lingadahalli area ( $13^{\circ} 36' : 75^{\circ} 51'$ ). This problem has now been investigated, and from a detailed microscopic study of these 'spots' and their relation to the main rock mass, evidence has been put forward to show that these are of the nature of amygdaloidal infillings and not due either to autoclastic phenomena or alteration of phenocrysts.

17. A note on the tuff of Wajrakarur, Anantapur District (Madras).

C. S. PICHAMUTHU and S. RAMACHANDRA RAO, Bangalore.

In view of the suggestion frequently made that the tuff of Wajrakarur ( $15^{\circ} 2' : 77^{\circ} 23'$ ) must be considered as the original matrix for the South Indian diamonds, a detailed study of this rock type was undertaken to find out its exact nature and probable similarity to the well-known diamondiferous Blue Earths of Kimberley. The rock is a typical tuff and often shows fragments of foreign rock such as the pink Gooty granite, hornblende-schist, etc., all cemented together by a glassy matrix which in some places presents a vitro-clastic texture. Under the microscope, sections of the rock show a general glassy matrix with a few crystalline grains here and there, chiefly of Microcline, Plagioclase Felspar and Hornblende. The general nature of the mineral contents and the entire absence of basic minerals like Augite and Olivine, together with the low specific gravity of the rock, suggest a tuff of andesitic composition, quite different from the matrix of the diamonds in the Kimberley mines.

18. Some structural features of the archaean rocks in the Sakoli Tahsil, Bhandara District (C.P.).

S. K. CHATTERJEE, Calcutta.

(Communicated by M. S. Krishnan.)

The archaean formations in the western and the central portions of the Sakoli Tahsil ( $21^{\circ} : 80^{\circ}$ ) appear to have witnessed at least three intense 'diastrophic storms' in the pre-cambrian era.



The original formations, which comprise both igneous and sedimentary rocks, had at first undergone metamorphism of the 'meso' grade, if not of a still higher order.

Regressive metamorphism in course of a later diastrophism reduced the prevalent order of metamorphism to the 'epi' grade. Further incidences of metamorphism are to be seen in the rotation of the garnet porphyroblasts in chlorite-muscovite-schists, the imposition of strain-slip, askew to foliation, in phyllites, and a general cross-folding which is revealed by ancillary pitches. Also, the area was cut up by an intersecting system of high-angle faults which strike roughly N.N.E.-S.S.W. and N.N.W.-S.S.E. respectively.

A third period of diastrophism was marked by the intrusion of granite. The granite crystallized under strong compressive stress, and was emplaced in the form of laccolith by means of a series of flows. Within the largest outcrop of granite, which is found towards the north-eastern part of the area, is exposed some coarse, grey, porphyritic epidote-biotite-granite, the 'streckung' of which shows that the granite magma must have flowed along the north-south direction. The Q-joints (tension joints) in the granite are filled with aplite and epidote-quartz-veins, and strike east-west. The fractures, caused by the compressional stresses in the country rocks during the intrusion, strike either N.-S. or N.W.-S.E. Many of these fractures were injected by the residual magma-liquor of the granite. Where the magma-liquor contained an abundance of 'mineralisers', e.g., boric acid, interesting mineralogical changes in the adjoining rocks were brought about, which led to a reversal from the 'epi' grade of metamorphism to 'meso' or 'kata' grade.

Perhaps even a fourth period of extensive diastrophism is indicated by a set of tension-fractures which strike north-south and are infilled by meta-dolerite. But evidence is at present inconclusive.

### METAMORPHISM.

19. On the origin and correlation of the manganiferous limestone and associated rocks of Sakarsanhalli Area, Kolar District (Mysore State).

M. B. RAMACHANDRA RAO, Bangalore.

A series of metamorphic rocks of the nature of garnetiferous-quartz-pyroxenites (Tarurites), Cumingtonite-schists, ferruginous-quartzites and manganiferous limestones from Sakarsanhalli area ( $12^{\circ} 47' : 78^{\circ} 13'$ ), Kolar District, have been carefully examined and mapped. From the evidences obtained both in the field and under the microscope, these metamorphic rocks are shown to be the result of acidic intrusions into hornblende-schists and amphibolites. The limestones have proved to be only secondary alterations of the pyroxenic rocks. The once suggested theory of sedimentary origin is shown to be untenable. It is also shown that these rocks are not of pre-Dharwar age but belong to the lower hornblende division of the Dharwars.

20. Contact metamorphism in limestones of the Mogok Series from the Mogok Stone Tract ( $23^{\circ} : 96\frac{1}{2}^{\circ}$ ).

A. K. BANERJI, Calcutta.

Two instances of contact metamorphism are discussed. In the first case a Felspar rock is intruded into limestone, coarsely crystalline Albite being the predominant Felspar in the rock. The contact rock consists of Nepheline, Diopside, Calcite, Felspar and Apatite. The genesis of the contact rock is shown to be the result of assimilation, the Nepheline



being formed through desilication of Albite material. In the other case, a pegmatite is in contact with the limestone. At the contact is developed a rock composed of Scapolite, Diopside, Felspar and Calcite. The contact rock is taken to be due to the interaction with the limestone, of magmatic material derived from the pegmatite.

## STRATIGRAPHICAL AND GENERAL (OLDER ROCKS).

### 21. The Palkanmardi conglomerate.

L. S. KRISHNA MURTHY, Hyderabad State.

At and near Palkanmardi ( $16^{\circ} 14' 3''$ ;  $76^{\circ} 47' 11''$ ), Deodrug Tehsil, Raichur District (Hyderabad State) near the junction-zone of the Dharwar schists and the peninsular gneisses, some interesting caught-up pebbles of gneisses and schists occur imbedded in an apparently igneous matrix. They are mostly rounded and water-worn and some of them are elongated. They vary in size from small pebbles to boulders about 1 foot or more in diameter. The paper discusses the geology of the area and the probable origin of the formation. Maps, photographs, micro-sections, and specimens illustrate the paper.

### 22. The geology of the country around Ghoriajor ( $22^{\circ} 3'$ ; $84^{\circ} 9'$ ) Gangpur State, Bihar and Orissa.

M. S. KRISHNAN and D. P. CHANDOK, Calcutta.

The rocks occurring in this area are referable to the Dharwars, and comprise members of the Gondite series, phyllites, mica-schists, crystalline limestones, gneissose granites and pegmatite. The schistose members are highly folded and dip towards the S.E. or E.S.E. at angles varying between  $30^{\circ}$  and  $60^{\circ}$ . The phyllites with the associated gondites seem to be the oldest rocks, followed by mica-schists and crystalline limestones. Tourmaline-bearing granite and pegmatite are intrusive into these. The gondites occur along a band about seven miles long and a quarter of a mile wide. They constitute several types in which combinations of the following minerals are present—Quartz, Microcline, Rhodochrosite, Spessartite, Rhodonite, Blanfordite, Winchite, Barite and Mangano-phyllite. The ores are mainly Braunite and Psilomelane with minor amounts of Pyrolusite.

Between 1909 and 1928 the area produced about 350,000 tons of ore, but the quarries were abandoned as, with increasing depth, underground mining would have become necessary if work were to be continued. The area is being re-explored by a Calcutta firm who were able to raise about 2,000 tons during 1930-31.

### 23. On the classification and correlation of the Champaner series of the Bariya State, Rewakantha Agency (Central India).

B. RAMA RAO, Bangalore.

Noting the salient features of the different groups of rocks of the northern extensions of Blanford's Champaner Series as developed in the Bariya State ( $23^{\circ}$ :  $74^{\circ}$ ), on lithological grounds and stratigraphic superpositions, the series has been classified into (1) The Dhanpur Schists ( $22^{\circ} 38'$ :  $74^{\circ} 6'$ ), (2) the Poyelli Limestone ( $22^{\circ} 28'$ :  $73^{\circ} 43'$ ), (3) the Baria Quartzites ( $22^{\circ} 42'$ :  $73^{\circ} 54'$ ), (4) the Dharua Limestone ( $22^{\circ} 27'$ :  $73^{\circ} 40'$ ), and (5) the Rajgad Shales ( $22^{\circ} 34'$ :  $73^{\circ} 39'$ ). Of these it is not clear whether the Dhanpur Schists have to be grouped among the Archaean Schists, or as the lowest members of the 'Champaner Series'. The rest



in their general lithological characters and order of superposition show a striking resemblance to the various groups of the Delhi System of Rajputana. The Poyelli Limestone corresponding to the Rialo Series, and the Baria Quartzites, Dharia Limestone and the Rajgad Shales to the Alwar Quartzites, Kushalgarh Limestone and the Ajabgarh Series respectively, indicate that the Champaner Series may in general be correlated with the Rialo Series and the Delhi System of Dr. Heron.

But the Poyelli Limestone members seem to have also their lithological equivalents among the limestones and the acidic schists in association with the Champion gneisses of Mysore, the constituents of the upper division of Dharwars.

It is doubtful whether the higher divisions of the Champaners, like the Baria Quartzites and the Rajgad Shales, have been represented therein or not.

It can only be said at present that the Champaner Series can be correlated with the Delhi System as classified by Dr. Heron in 1917, and also with a *part* of the upper Dharwars of Mysore. The series can neither be correlated with the Aravallis, nor with the whole of the Dharwars as suggested by some geologists.

#### 24. Some studies in the geology of the area west of Banganpalli, Banganpalli State (Madras).

C. S. PICHAMUTHU and M. R. SRINIVASA RAO, Bangalore.

The paper gives a detailed account of the geology of the area about 6 miles west of Banganpalli ( $15^{\circ} 18' : 78^{\circ} 14'$ ), and from certain evidence detailed in the paper, the probable existence of an east-west fault line, almost parallel to the Jurreru river, is suggested.

#### 25. Notes on the geology of Mt. Diamir (26,620 ft.) (Nanga Parbat), North-west Himalaya, Kashmir.

D. N. WADIA, Calcutta.

Nanga Parbat ( $35^{\circ} 14' : 74^{\circ} 35'$ ), the culminating peak of the Punjab Himalaya, is not a peak on the central axis of the Great Himalaya Range, but it stands out as a solitary eminence to the north of that axis as a mighty spur. It presents stupendous, bare, rocky precipices to the south and south-west, but to the north, the aspect is rather tame, though this flank ascends 22,500 ft. directly from the Indus bed, within barely 17 miles. This slope is concealed under 100 sq. miles of snowfields, drained by four glaciers which descend nearly 8,000 ft. below the snow-line.

Above 15,000 ft. level, the mountain is almost inaccessible to field geologists, the wall-like precipices of the south, rising sheer 13,000 ft. from the Rupal valley and the unrelieved snow-cap on the north, alike forbid approach. For this portion, the enormous stretches of moraines and the fresh, frost-bitten rock-debris continually shed by the avalanches, are the only means of investigation. Below the snow-line, however, the geological structure as well as composition is laid bare in a series of fine exposures, well seen in the naked cliffs facing the Indus and the Astor valleys.

From these, the geology of Nanga Parbat is found to be of great simplicity. It is composed almost entirely of finely schistose, streaky biotite-gneiss with interbedded coarsely re-crystallised marble, graphite-schist, etc., well-stratified and having a persistent dip to the north-west; these are traversed by thick basic black epidioritised dolerite sills and dykes, now represented by massive amphibolite and hornblende-schist. The present writer has no doubt that the biotite-gneiss is a paragneiss, a transformation-product of original pre-Cambrian sediments (his Salkhala series) which constitutes the country-rock of the surrounding region.



Through this basement complex are thrust sheets and dykes of acid granite-gneiss of a later intrusive phase. In the Tarshing valley and further south-east near Rattu, the Nanga Parbat gneiss gradually passes into less metamorphosed Salkhalas in which all the typical elements are easily recognised.

The tectonics of the Nanga Parbat region is discussed in relation to the syntaxial angle of the North-West Himalaya.

## STRATIGRAPHICAL AND GENERAL (ARYAN).

### 26. On the flints and cherts of the Niniyur Stage (II).

L. RAMA RAO and C. PRASANNAKUMAR, Bangalore.

In a paper communicated to this section of the Congress in 1930, the authors have generally established the fact that the several bands of flints and cherts of the Niniyur Stage, are all the result of silicification of previous organic limestones. The present paper is a more intensive study of the flints from a particular area, near Sainthoray ( $11^{\circ} 15' : 79^{\circ} 13'$ ), with a view to resolving them further into definite types based on the exact nature of the parent rock and subsequent differences in the type of silicification.

### 27. On the mode of origin of the Lameta limestone of Jhabu, Bariya State (Central India).

B. RAMA RAO, Bangalore.

Due to Dr. Fermor's suggestion (*Rec. Geo. Surv. Ind.*, Vol. XLIII, page 32) that many of the so-called Lameta Limestone outcrops of Central India might be of metasomatic origin, as he found to be the case of the infra-trappean limestones of the Chhindwara District, the Lameta limestone band of Jhabu ( $22^{\circ} 40' : 74^{\circ} 11'$ ) was carefully examined. All the evidence available in the region points out that the main mass of the limestone could not have originated due to replacement of any rock by calciferous solutions, either during the pre-trappean or post-trappean period. By its definite horizon underlying the sandstone members of the 'Lameta series' and overlying unconformably the crystalline schists, and by the characteristic micro-textures of the slides of many of its specimens, the rock is believed to have a true sedimentary mode of origin.

In the same region are other insignificant isolated patches of calciferous rocks formed by diverse methods which by their infra-trappean position might be mistaken as variant phases of the true limestone. Instances of such pseudo-Lameta calciferous rocks have been noted for comparison.

### 28. The application of the Nappe Theory in the Himalayas.

S. K. ROY and B. BHARGAVA, Dhanbad.

When mapping Mandi State ( $31\frac{1}{2}^{\circ} : 77^{\circ}$ ), Punjab, geologically, one of the authors found slicken-sided masses of pink dolomite marble, probably of Blaini age, lying unconformably in irregular and isolated north-south strips on the unmetamorphosed Tertiaries of the area, at an altitude of about 4,000 ft. The rocks are lying among these without roots. Similar rock is found, more or less at the same altitude in autochthone condition only after one has gone more than 16 miles towards east. No trace of the rocks could be seen in the intervening country occupied by hills of granite, slates and quartzite more than 7,000 ft. high. The only plausible explanation of the above phenomena is that the dolomite has been everthrust as in the case of Nappes of the Alps.

The paper includes the first geological map of Mandi State (scale 1 inch=2 miles).



29. Geology of Mandi Salt Deposits, Mandi State (Punjab).  
S. K. ROY and B. BHARGAVA, Dhanbad.

Mandi State ( $31\frac{1}{2}^{\circ}$ :  $77^{\circ}$ ) contributes about 3 per cent. of the total salt manufactured in India. Its geology is very complicated and has not been studied before. During a joint investigation of the materials collected by one of them, the authors came to the conclusion that the salt is of Tertiary age.

The paper includes original detailed geological maps of the salt areas and a few unpublished photographs of the salt mines.

30. A note on the Quilon limestone.

C. S. PICHAMUTHU and C. PRASANNAKUMAR, Bangalore.

Though the probable presence of a bed of limestone below the laterite round about Quilon ( $8^{\circ} 53'$ :  $76^{\circ} 36'$ ), Travancore State, was suggested so far back as about 1850, yet none of the subsequent observers were able to get at the rock *in situ* but based their conclusions regarding the nature of what they called the Quilon limestone only on the study of a few stray boulders found round about Quilon. This paper records the rediscovery of this limestone below the carbonaceous beds of the Warkalay formation and its *in situ* occurrence has been proved in an excavation about 8 miles south-east of Quilon. The limestone is highly fossiliferous and two types of corals, several genera of molluscs, some foraminifers and a fossil-crab have been recorded, all of which suggest a middle tertiary facies.

### SEDIMENTARY PETROLOGY.

31. Petrology of some Barakar sandstones occurring in Gangpur State, Bihar and Orissa.

M. S. KRISHNAN, Calcutta.

Barakar sandstones overlying Dharwarian metamorphic rocks occur in the south-western part of Gangpur State ( $22^{\circ}$ :  $84^{\circ}$ ). They have a low ( $10^{\circ}$ – $20^{\circ}$ ) southerly or south-westerly dip, and their contact with the metamorphics seems to be one of original sedimentary deposition. They are generally felspathic and contain ferruginous matter, Muscovite and occasional Tourmaline.

Heavy minerals were separated from four specimens. Three of these showed very abundant Tourmaline—over 95 per cent.—and small quantities of Magnetite and Ilmenite, Epidote, Garnet, and Rutile. The fourth specimen was an exceptionally pure sandstone with matrix of white clay. The small amount of heavy minerals obtained from this contained iron ore, Zircon, Rutile, Hornblende, Tourmaline, Actinolite, and traces of Monazite, Kyanite, Staurolite and Garnet.

The source of the sediments seems to be the granitic gneisses and mica-schists occurring to the north and north-east, especially as these are rich in Tourmaline and also contain the other minerals mentioned above.

32. The heavy mineral assemblages of white clay and ochres associated with laterite of Sohawal State ( $24^{\circ} 25'$ :  $80^{\circ} 45'$ ), C.I.

N. L. SHARMA and S. PURKAYASTHA, Dhanbad.

The white clay and red and yellow ochres of Sohawal State show almost exactly similar heavy mineral assemblages, characteristic minerals being Kyanite, Staurolite, Rutile, Garnet, Tourmaline, and Zircon. The frequency of all the minerals and descriptions of the more important ones have been given in the paper.



It is interesting that most of these minerals are totally absent in the Upper Rewah and Upper Bhandar sandstone beds underlying the laterite in which the high grade clays occur.

### COAL.

33. Note on the occurrence of coal seams near Karmatanr in the Rajmahal Hills, Santal Parganas (Bihar).

N. N. CHATTERJEE, Calcutta.

During his short visit in the Rajmahal hills the author came across coal seams in the Barakars at the foot of the hills near the village Jilbari ( $24^{\circ} 51' : 87^{\circ} 24'$ ) some five miles from Karmatanr in the Santal Parganas District. The author points out in the paper that in the Geological map of the Rajmahal hills published by the Geological Survey of India in 1877 there is no indication of the development of the Barakars in that area and that no mention has been made by Ball in his memoir of the occurrence of coal seams there. The coal seams occur intercalated between beds of very much decomposed white felspathic sandstone and are worked locally by simple methods of quarrying. The quality of coal is also discussed in the paper.

34. Action of solvents on some Indian coals. IV.

N. N. CHATTERJEE, Calcutta.

In the paper the author has embodied the result of his study of the action of Pyridine and Chloroform on some Jharia coals. The specimens were obtained from seams Nos. X, XI, XII, XIII, XIV, and XV. All of them are caking coals and in quality they do not differ to a very great extent. The amounts of the alpha, beta and gamma compounds in these coal specimens were determined quantitatively and the analytical results show that the amounts of the pyridine-extract in the different specimens vary within wide limits. In the case of seam No. XIV the amount of pyridine-extract was very small whereas that of seam No. XII came to about 11 per cent. of the coal substance. The percentage of the gamma compound in the coal samples also varies greatly. The relationship between the amounts of these extracts and the carbon-hydrogen ratio is discussed. The effect of oxidation of the coal substance on the caking property and the behaviour of the oxidised coal substance towards the solvent action is also dealt with in the paper.

### GEOPHYSICAL.

35. A survey of the Punjab by the Torsion balance.

N. K. BOSE, Lahore.

A few isolated cases of this survey work were read before the Congress last year. This work has been completed now and a report on this work will be published from the Punjab Irrigation Research Institute. A few cases of geological interest will be put forth in this paper:—

- (1) Continuation of the subterranean heavier layer below the Salt Range—does it help to clear the ideas about origin of the Salt Range?
- (2) Is the subterranean heavier layer a continuation of the outcrops at Kiranas ( $31^{\circ} 58' : 72^{\circ} 43'$ ), Chiniot ( $31^{\circ} 43' : 72^{\circ} 59'$ ), Sangla ( $31^{\circ} 43' : 73^{\circ} 22'$ ), and Shakkot ( $31^{\circ} 34' : 73^{\circ} 29'$ )?



**WATER SUPPLY.**

36. Salinity of the underground water and occurrence of Brine in parts of Raichur Do-ab ( $16^{\circ} : 77^{\circ}$ ), Hyderabad State.

S. K. MUKHERJI, Hyderabad State.

Parts of Raichur Do-ab, Hyderabad State, are saliferous. The indigenous salt industry has been carried on from time immemorial both from brine and saline efflorescence. In the course of operations of the Well Sinking Department, it has been noticed that the younger acidic representatives of the Pink Series of Peninsular Gneisses of the area, either in contact with the Dharwar Schists, or independently of them in the neighbourhood, have yielded saline water. The paper discusses the distribution, mode of occurrence and the probable origin of salinity, and gives complete analyses of samples.

**PALAEONTOLOGY.**

37. On a limestone from the Pondicherry Cretaceous.

L. RAMA RAO, Bangalore.

The paper gives a complete description of a very interesting type of organic limestone, forming one of the members of the Pondicherry Cretaceous and records the extensive occurrence in sections of this limestone, of *Lithothamnion*—an alga which was only recently discovered by the author in the Niniyur beds of the Trichinopoly Cretaceous. From a study of the fossils occurring in this limestone, the question of the probable correlation of the rocks of the Pondicherry area with those of the Trichinopoly Cretaceous, is discussed.

38. Some radiolaria from the Trichinopoly Cretaceous.

L. RAMA RAO, Bangalore.

The paper records the occurrence of Radiolaria from the Trichinopoly Cretaceous rocks and embodies a brief descriptive account of some of the more important types from the phosphatic nodules of Utatur ( $11^{\circ} 4' : 78^{\circ} 35'$ ). Several genera mostly belonging to the Spumellaria have been described and illustrated. The paper is thus a first contribution to a study of the South Indian Cretaceous Radiolaria, about which we now know so little.

39. On the age of the Dudkur fossiliferous beds, Madras Presidency.

H. C. DAS-GUPTA, Calcutta.

The fossiliferous beds at Dudkur ( $17^{\circ} 2' : 81^{\circ} 38'$ ) were first recognised by King in 1880 who relegated them to the infra-trappean. The beds were visited by the author with a party of students and fossils collected. A preliminary examination of the fossils reveals the presence of *Venericardia Beaumonti*, d' Archiac. The age of the beds is discussed and the author concludes that the beds should be regarded as inter-trappean and not infra-trappean.

40. On the occurrence of lithothamnion in the eocene beds of the Salt Range (Punjab).

H. C. DAS-GUPTA, Calcutta.

A description of the specimen.



## 41. Additional fossil localities in the Upper Tertiaries of the Garo Hills, Assam.

P. EVANS, W. B. METRE, and B. H. SINGH, Digboi.

In view of the rarity of fossils in Assam special interest attaches to the two fossil beds found by Mr. Pinfold in the southern portion of the Garo Hills (*Rec. Geol. Surv. Ind.*, Vol. L, Part 2). A third fossil locality having recently been found by Dr. Fox, the junior authors, working under the direction of Messrs. Sale and Evans for the Burmah Oil Company were instructed to search for additional localities in this area. Nineteen new fossil occurrences were discovered, nine near Baghmara ( $25^{\circ} 12' : 90^{\circ} 38'$ ) and ten north of Dalu ( $25^{\circ} 13' : 90^{\circ} 13'$ ).

The nummulite-bearing Eocene limestone and shales are unconformably overlain by Upper Tertiary beds. The lower portion of these is mainly alternations of sandstone and shale and the higher portion, in which the fossil beds occur, is made up of sandstones, grits, conglomerates, sandy shales and mudstones. From the work of Messrs. Vredenburg, Mukherjee and Eames the fossil beds are to be regarded as approximately Upper Gaj or Burdigalian.

The paper describes in detail the position of all the better localities discovered by the junior authors and summarizes the less important localities, and is accompanied by maps which should enable other workers to identify the position of each bed.

The writers are indebted to Messrs. The Burmah Oil Company for permission to publish this paper.

## 42. The Kanchanpur fossil bed.

H. M. SALE, Badarpurghat.

Owing to the rarity of fossils in the Upper Tertiaries of the Surma Valley a special interest is attached to the fossil bed at Kanchanpur ( $24^{\circ} 39' : 92^{\circ} 31'$ ), to which reference was first made in the General Report of the Geological Survey of India for 1927. In this locality in Cachar a comparatively rich marine fauna of Lower Miocene age occurs in a thin fossiliferous bed which is placed stratigraphically in the uppermost beds of the Bhuban Stage.





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# INDIAN SCIENCE CONGRESS.

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Twentieth Annual Meeting,  
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## ABSTRACTS OF PAPERS.

Section of Chemistry.

*President :—Dr. P. Neogi, M.A., Ph.D., I.E.S.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Chemistry.

### *Abstracts.*

#### 1. Natural gas from Assam and Burma.

G. P. KANE and K. R. KRISHNASWAMI, Bangalore.

A number of samples of natural gas from the Assam and Burma oil-fields has been examined with special reference to their helium content. The methods of analysis and the results are given.

#### 2. An examination of a very insoluble phosphate extracted from Monazite obtained from Orissa.

C. B. ROY and S. B. ROY, Patna.

While analysing Monazite in the black sands of Orissa, a very refractory phosphate was left behind after repeated bisulphate fusions, which was believed to be either wholly salt of zirconium or some new element or mixture of both. A sample of crude chloride prepared from this phosphate was found by Dr. Hevesy of Copenhagen to contain about 2% of Hafnium discovered in 1923. A short report of this work was published in *Welfare*, India, May, 1925.

The chloride after further purification was again examined. Equivalent weight determination from chloride and sulphate was attempted. Atomic weight deduced, gave values ranging from 99 to 107.5. A report on the spectroscopic examination of the purified salt is appended. Prof. Hopkins of Illinois University, after examination in his laboratory of a sample of salt prepared by us, confirmed our previous conclusions of the salts originating from zirconium. Some characteristics, however, of the salts remain unexplained on the assumption that it is a pure zirconium salt.

#### 3. The mechanism of hydrolysis of magnesium boride.

R. C. RAY and P. C. SINHA, Patna.

Magnesium boride was prepared by heating rapidly to red-heat an intimate mixture of freshly prepared and finely powdered boron trioxide and magnesium. The mixture of magnesium boride and oxide thus obtained was powdered and added, in small quantities at a time, to a mixture of absolute alcohol and hydrochloric acid of different strengths kept in a bottle provided with a stirrer and immersed in crushed ice. Hydrogen was rapidly evolved and a white powder, which was free from magnesium oxide and free boric acid, separated. The compound is inactive towards both cold and hot water and has the composition  $Mg_3B_2(OH)_6$ . This appears to be the main product of hydrolysis of magnesium boride. There is, however, some evidence of the formation of an intermediate compound, but it has not yet been possible to isolate it.

#### 4. Fluoberyllates and their analogy with sulphates.

Part V.—Double fluoberyllates of some of the bivalent metals with thalious fluoberyllate.

NIRMALENDUNATH RÂY, Rajshahi.

Preparation of thalious fluoberyllate has already been described (Rây, *Zeit. anorg. chem.*, 201 [1931], 297). Equimolecular quantities of



this salt and a fluoberyllate of a bivalent metal such as Ni, Co, Zn, etc., were dissolved in the minimum quantity of water and allowed to crystallise. Crystals of the general formula  $Tl_2 BeF_4 M^I BeF_4 \cdot 6H_2O$  were obtained. These were isomorphous with the corresponding double sulphates described in a previous publication (Rây, *Zeit. anorg. chem.*, 206 [1932], 200).

5. Fluoberyllates and their analogy with sulphates. Part VI.  
—The Hydrazinofluoberyllates.

NIRMALENDUNATH RÂY, Rajshahi.

The Hydrazinofluoberyllates analogous to the hydrazinosulphates of Franzen and Mayer have been prepared and their properties studied.

6. Dithiosulphato di-ethylenediamine cobaltates.

PRIYADARANJAN RÂY and S. N. MAULIK, Calcutta.

The preparation of a new series of complex cobaltates—sodium, potassium and thallium salts of dithiosulphato-di-ethylenediamine cobaltic acid—has been described and their properties studied in the present paper. With the two thiosulphato groups, each occupying one co-ordination position, these salts, as is well-known, should exist in cis-trans isomeric forms. This has been proved by preparing both the stereo-isomeric forms of the sodium salt, which differ widely in their colour, solubility, and other physical properties.

Attempts are being made to resolve the cis-modification of the salt into its optical antipodes.

7. Simple and complex iodates of tetravalent lead.

PRIYADARANJAN RÂY and HARIBOLA SAHA, Calcutta.

In continuation of our previous work on iodates of tetravalent tin and titanium, we have now been able to prepare tetra-iodate of lead, di-hydroxo-tetra-iodato plumbic acid, hydrated hexa-iodato plumbic acid and its alkali salts. The properties of the compounds have also been investigated.

8. Substituted complex cyano-cobaltates.

PRIYADARANJAN RÂY and T. GUPTA CHOWDHURY,  
Calcutta.

Starting from di-sulphito-tetracyano-sodium cobaltate described by Rây and Chackrabarty, silver, lead, and alkali salts of a new type of complex di-aquo-tetracyano-cobaltates have been prepared and their properties studied. The highly soluble alkali salts are characterised by the unusual property of being changed into an insoluble modification on drying at the ordinary temperature.

9. The effect of tannin on the physical properties of clays.

P. Y. NARAYANA, H. E. WATSON, and M. A. GOVINDA RAO,  
Bangalore.

Experiments have been conducted to ascertain if the commercial sodium tannate now used to reduce the viscosity of mud used for well-boring can be replaced by tannin materials of indigenous origin. It has been found that an extract of *Cassia auriculata* either alone or with the addition of sodium hydroxide behaves in a similar manner to sodium tannate and is in some respects more satisfactory.



## 10. Action of nitric acid on tin.

G. S. KASBEKAR, Bombay.

The reaction between nitric acid and tin under different conditions of concentration and temperature has been systematically studied by the estimation of all the following products formed during the reaction, viz.:—

Nitrate, Nitrite, Stannous and Stannic salt, Hydrazine, Hydroxylamine and Ammonia.

Estimation of the gases formed during the reaction is proceeding. It is found that in addition to the marked changes in the reaction products due to alterations in concentration, temperature, etc., certain catalysts greatly influence the velocity of reaction as also the nature of the products formed. Some catalysts have been observed to completely inhibit the reaction between nitric acid and tin.

## 11. Heat of formation of potassium tri-iodide.

S. S. JOSHI and SUBRAMANIAM IYER, Benares.

Based on experiments on the influence of temperature on the distribution coefficient of iodine between toluene and water, the latter containing varying proportions of potassium iodide, it has been deduced that the heat of  $KI_3$  formation is very small in the temperature range  $8^{\circ}$ – $40^{\circ}C$ .

## 12. Formation of Bromine-chloride.

S. ANWAR-ULLAH.

The preparation of the bromine chloride was first claimed by Balard in 1826 and was confirmed by Löwig in 1829. Since then several observers have failed to find any evidence in favour of its existence. Recently photometric work and also the phenomena encountered in certain organic reactions, have definitely shown that bromine-chloride exists in equilibrium with bromine and chlorine. The author has brought about further proof of the formation of the bromine-chloride by the establishment of the equilibrium constant for the halogens and their compound and through the study of bromine-chloride hydrate.

## 13. Conductivity of bromine-chloride.

S. ANWAR-ULLAH.

Experiments have been made to test whether the solutions of bromine-chloride mixtures also act in the same way as that of iodine-chloride and iodine-bromide in nitrobenzene, where the iodine separates at the cathode, for by analogy bromine-chloride might reasonably be expected to be ionised to some extent. It has been observed that solutions of bromine-chlorine mixtures do conduct. The addition of chlorine to bromine dissolved in pure dry nitrobenzene lowered the resistance of the latter solution to about one-third of its previous value. When solutions of the halogens were kept in a dish and two platinum electrodes were connected through a milli-ammeter to the mains the instrument moved over several divisions and a gas was evolved from the anode. No gas was detected at the cathode.

It seems difficult to interpret these observations except by the assumption that bromine-chloride is formed in solution and dissociates to some extent into positive bromine ions and negative chlorine ions.



## 14. Restoration of bronze images.

S. PARAMASIVAN, Madras.

The mechanism of corrosion and restoration of bronze images is extremely complex. Chemical methods of restoration have serious defects, especially in cases of heavily corroded bronzes. In restoring very heavy bronzes like the ones in the Government Museum, Madras, one finds it extremely difficult either to handle the bronze with ease or to regulate the chemical reaction during the progress of restoration. In these respects, the electrolytic or the Fink method has many advantages, and is the only effective method for eliminating 'Bronze Disease'. The Fink method, which has been in regular use in some of the prominent American Museums for restoring very small bronzes, has now been extended here for restoring heavy and large sized bronzes at the Government Museum, Madras. In this connection, the experimental technique has been developed here.

## 15. Attempts to synthesise p-diphenylene. Part II.

V. C. PAREKH and P. C. GUHA, Bangalore.

Some further work has been done in continuation of paper No. 134 (*Indian Science Congress Abstracts, Section of Chemistry, 1932*) by way of gathering facts for the elucidation of the structure of p-diphenylene-dimonosulphide. The paper embodies results obtained in our attempts to synthesise the above compound from pp-di-amino-di-phenyl-sulphide as also by the action of p-di-brom-benzene on the di-sodium derivative of p-di-mercaptan of benzene. The effect of other groups like  $(CH_2)_n$ , CO, and  $(NH)_n$  in bridge formation between the two pairs of para carbon atoms of two benzene molecules is under investigation.

## 16. Action of ammonia and urea on carbo- and oxalyl-diurethane.

P. C. GUHA, Bangalore.

In continuation of the work described in paper No. 143 (*Indian Science Congress Abstracts, Section of Chemistry, 1929*) it has been found that urea reacting with oxalyl-diurethane gives, besides carbo-oxalyl-diurea and oxalyl-diurea four more compounds, viz. (a) allophanic ester, (b) carbethoxyoxamide  $NH_2-CO-CO-NH-COOEt$ , m.p.  $157^\circ$ , (c) dicarbethoxy-oxalyl-diurea m.p.  $230^\circ$ , and (d) a compound m.p. above  $330^\circ$  of the composition  $C_5H_{10}O_5N_6$ . In the course of the preparation of oxalyl-diurea from the urethane by the action of ammonia a compound m.p.  $235^\circ$  of

the structure  $\begin{array}{c} CO-NH-CO \\ | \\ CO-NH-CO \end{array} > NH$  has been isolated. Carbodiurethane gives the monoamide (m.p.  $190^\circ$ ) with ammonia; and two compounds, viz., allophanic ester and  $CO < \begin{array}{c} NH-CO-NH-CO-NH_2 \\ NH-CO-NH_2 \end{array}$  (m.p.  $240^\circ$ ) with urea.

## 17. On a new method of synthesis of norpinic acid.

P. C. GUHA, Bangalore.

In the paper are described experiments conducted in the process of effecting condensation of brom- and chlor-acetol with methylene dimalonic ester on the one hand and isopropylidene dimalonic ester with methylene iodide on the other; and the conversion of the resulting 1:3-methylene: isopropylidene-2:4-dimalonic ester into the corresponding



tetracarboxylic acid. The latter on being freed from two molecules of carbon dioxide is expected to give norpinic acid (cf. Kerr, *J. Am. Chem. Soc.*, 1928, 51, 614; Clemo and Welch, *Trans.*, 1928, 2621; Ganguli, *J. Indian Inst. Sci.*, 1922, 23; Kotz, *J. Pr. Chem.*, 1907, 75, 494). Considerable improvement has been effected in the methods of preparation of chloracetol, bromacetol, and isopropylidene-malonic ester.

### 18. On the synthesis of uric acid from nine-membered poly-peptides.

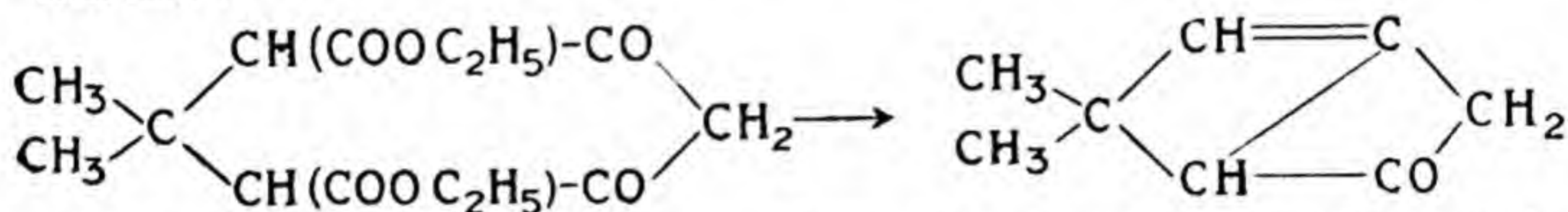
P. C. GUHA, Bangalore.

Though carbo-oxalyl-diurea and carbo-ethylene-diurea and what appears to be desoxy-uric acid (formed from the latter) have been synthesised and reported in the abstracts of the previous years; the actual synthesis of uric acid has not so far been possible to achieve due to the difficulties involved in the synthesis of carbo-glycolyl-diurea. The product reported in the *Indian Science Congress Abstract, Section of Chemistry*, No. 50 of 1930 to be carbo-glycolyl-diurea has now been found to be not a pure substance. The present paper embodies the results of a large number of experiments done so far with the object of preparing carbo-glycolyl-diurea and allied substances from which uric acid can be easily obtained. The action of urea and biuret has been studied upon carbethoxy-glycine ester, carbethoxy-glycineamide, glycolyl-diurethane, hydantoin ester and hydantoinamide under various conditions of experiments and quite a large number of compounds have thus been isolated.

### 19. Constitution of Isophorone.

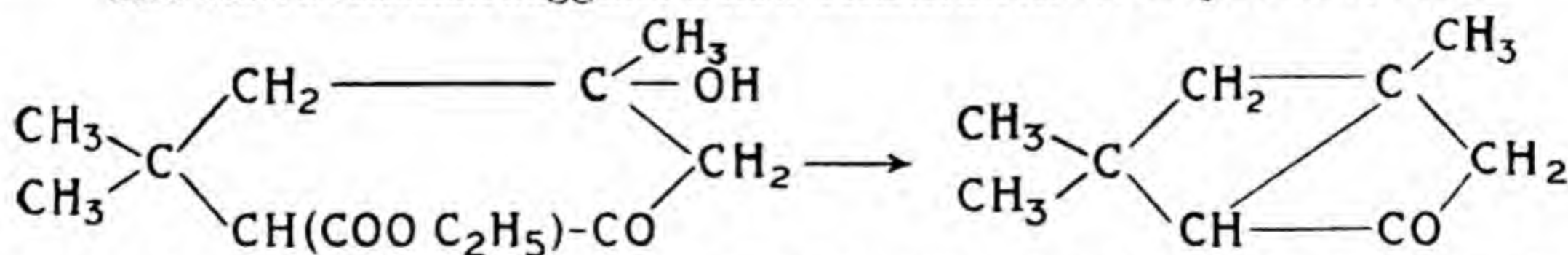
P. S. MAYURANATHAN, Bangalore.

A dicyclohexenone (*Indian Science Congress Abstract*, 1932, *Section of Chemistry*, p. 33) was discovered during the course of the following reaction :



Possibly, enolisation had taken place and dehydration subsequently resulted due to the presence of an active hydrogen para to the hydroxyl. The constitution was proved by preparing derivatives and also by bromination, hydrolysis, oxidation and reduction.

The above reaction suggests a new constitution for isophorone, viz.—



quite distinct from the already accepted tautomers proposed at different times by different authors.

The following evidences have so far been collected :—

- Isophorone is polymerised and a dimer is obtained.
- Isophorone is reduced by Clemensen method and a hydrocarbon  $\text{C}_{18}\text{H}_{32}$  is obtained. The constitution is being studied.
- The principle of the formation of isophorone is discovered in the necessity for the presence of the active hydrogen para to the hydroxyl. The moment it is substituted, there is



inhibition of dehydration and consequent hydrolysis. With methyl-aceto-acetic and propionyl-propionic esters the main products are the  $\alpha$ -esters, but with aceto-acetic ester only isophorone and the dehydro-ester are discovered.

## 20. On dicyclohexenones.

P. S. MAYURANATHAN, Bangalore.

Isobutylidene- and cyclopentylidene-malonic esters have been respectively condensed with aceto-acetic ester and the corresponding dicyclohexenones isolated. The constitution of the dicyclohexenones is proved on similar lines with the dimethyl analogue. A comparative study of their stability is being carried out. Work is extended to the higher homologues in the aliphatic and hydro-aromatic series.

## 21. On resorcin-esters.

P. S. MAYURANATHAN, Bangalore.

The following new resorcin esters have been synthesised :—

1. Ethyl cyclohexane-1-phenyl-3 : 5-diketo-4-methyl-2 : 6-dicarboxylate.
2. Ethyl cyclohexane-1 : 1 : 2-trimethyl-3 : 5-diketo-6-carboxylate.
3. Ethyl cyclohexane-1 : 1 : 4-trimethyl-3 : 5-diketo-2 : 6-dicarboxylate.
4. Ethyl cyclohexane-1 : 1 : 4-trimethyl-3 : 5-diketo-6-carboxylate.

During the formation and hydrolysis of some esters, interesting results are obtained which are being investigated. A generalisation for the condition controlling the internal dehydration in resorcin-esters is discussed.

## 22. Substitution in resorcinol derivatives : chlorination of nitro-derivatives of $\beta$ -Resorcyaldehyde.

M. SESA IYENGAR and K. SANTANAM, Bangalore.

It has been pointed out that during the bromination of certain nitro-derivatives of  $\beta$ -Resorcyaldehyde an intra-molecular rearrangement takes place. (*J. Chem. Soc.*, 1932, 524.) The action of chlorine on the compounds referred to, is now being studied with a view to find whether such a rearrangement would take place during chlorination also. As a result of study, we have prepared 3-nitro-5-chloro-2-hydroxy-4-methoxy-benzaldehyde (m.p. 115-116°) and 5-nitro-3-chloro-aldehyde (m.p. 130-131°). Further chlorination of either the 3-nitro- or the 5-nitro-monochloro-derivative did not yield any definite compound. The bromination of the 5-nitro-3-chloro-2-hydroxy-4-methoxy-benzaldehyde yielded, however, a golden yellow substance (m.p. 120°) indicating an ortho-phenolic structure. Further work is in progress.

## 23. Resolution of co-ordinated inorganic compounds. Part I. d- and l-tri-ethylene-diamino-zinc chloride, bromide, iodide and sulphate.

P. NEOGI and GOPAL KRISHNA MUKHERJI, Calcutta.

Attempts have been made to resolve tri-ethylene-diamino-zinc salts and for this purpose the reagents chosen have been d-tartaric acid, d-camphor-sulphonic acid, sodio-camphor-nitronate, and nitro-camphor.

The d-tartrate, d-camphor-sulphonate of the complex have been prepared and fractionally crystallised. On removal of the active residue, however, the resulting solution becomes inactive.



Using sodium camphor-nitronate and nitro-camphor positive results have been obtained and the *d*- and *l*-varieties of the chloride, bromide, iodide and sulphate have been obtained. The solutions, however, become racemic on keeping.

Further work is in progress.

#### 24. Mutarotation. Part I.—Turmerol.

BIJOOR SANJIVA RAO, Bangalore.

The rate of transformation of the turmerol alone and of its solutions in alcohol and glacial acetic acid has been studied. An explanation for the change has been offered.

#### 25. Mutarotation. Part II.—Mono- and bicyclic terpenes.

BIJOOR SANJIVA RAO, Bangalore.

The change in rotation, following the changes due to oxidation in these compounds, have been recorded. To decide, if the change in rotation is due entirely to oxidation effects, the optical activity of samples, in which oxidation and polymerisation changes have been nearly inhibited, is being studied.

#### 26. Studies in Walden inversion. Part I.

V. ANNA RAO and P. C. GUHA, Bangalore.

Cec. L. Horton's rule (*Chem. News*, 1913, 108, 37), which claims to predict the direction of reaction in Walden inversion processes from the number of free carboxyls present in any compound, has been tested with reference to a large number of known cases and the following facts brought to light :—

- (a) Horton has overlooked about one hundred cases then known, taking only twenty-six examples as the basis of his rule.
- (b) There are about forty exceptions among approximately one hundred and forty cases.
- (c) There are several errors arising out of attempts to determine the direction of reaction in Walden inversion processes on the basis of change of *sign* of the active products.
- (d) So far as the successive use of certain reagents to produce either the original acid or its enantiomorph is considered (e.g. NOBr and NH<sub>4</sub>OH, etc.), the available data go definitely against his generalisation.

#### 27. Studies in Walden inversion. Part II.

V. ANNA RAO and P. C. GUHA, Bangalore.

Attempts have been made to convert *meso*-tartaric acid into one of the active varieties of tartaric acid by the application of Walden inversion process to only one of its asymmetric centres. The reverse process, viz. the conversion of *dl*- $\beta$ -chloromalic acid into *meso*-tartaric acid is known and is evidently due to Walden inversion taking place in one-half of the molecule. Successive halogenation and hydroxylation of *meso*-tartaric acid and its mono- and di-ethyl esters have furnished interesting results and thrown additional light on Horton's generalisation.

#### 28. On asymmetric synthesis of organic sulphur compounds. Part II.

V. C. PAREKH and P. C. GUHA, Bangalore.

In continuation of the work reported last year (*Indian Science Congress*, 1932, Abstract No. 130, Section of Chemistry) attempts have



been made to achieve asymmetric synthesis of organic sulphur compounds by condensing menthyl- $\beta$ -bromopropionate with propyl-methyl-sulphide, and butyl-methyl-sulphide, but the resulting products, on being freed from the active menthyl group by hydrolysis, have been found to be inactive.

29. Studies in abnormal optical rotation. Parts VI and VII.

M. S. KOTNIS, BIJOOR SANJIVA RAO, and P. C. GUHA,  
Bangalore.

Camphoryl-mustard oil and camphor quinone have been condensed with carbo-, oxalyl-, malonyl-, succinyl-, glutaryl-, and adipyl-dihydrazides and meta- and para-phthalyl-dihydrazides and optical activity of the products obtained has been studied in a few solvents. The effect of the carbonyl group, methylene group, and the benzene ring on the optical activity in this series of compounds has been determined.

30. Rotatory dispersion in the terpene series. Part II.

R. PADMANABHAN and S. K. K. JATKAR, Bangalore.

In continuation of previous work, the following substances have been prepared pure and their rotatory dispersion measured in the ultra-violet: (1) d-pinene, (2) d-limonene, (3) d- $\Delta_3$ -carene, (4) d- $\Delta_4$ -carene, (5) d- $\alpha$ -thujene, (6) d-sabinene, (7) l-camphene. It has been found that the optical rotation can be measured as far as  $\lambda 3000$  when a thickness of 2.5 cm. of the pure liquid is employed. From the results obtained, it has been found that (1) limonene and pinene possess simple rotatory dispersion, (2)  $\Delta_3$ -carene,  $\Delta_4$ -carene and  $\alpha$ -thujene possess complex dispersion, (3) sabinene and camphene possess anomalous dispersion. The anomaly for these two substances can be satisfactorily explained by the theory of induced asymmetry put forward by Lowry and Walker and appears to be due to the occurrence of a semi-cyclic double bond in close proximity to the asymmetric carbon atom.

31. Geometrical inversion in light. Part II.—Inversion of bromo-cinnamic acids.

B. K. VAIDYA, Bangalore.

Quantum efficiency measurements of the mutual inversion of the *cis*- and the *trans*-forms of  $\alpha$  and  $\alpha\beta$ -bromo-cinnamic acids in aqueous solutions, in radiations of  $313\mu\mu$  and  $253\mu\mu$  wavelengths have been carried out. In presence of light an equilibrium is established in the system with about 85–90 per cent. of the *cis*-form. Small variations have been observed with change in concentration. The kinetics of the change indicate that the reaction is of zero order and the rate is proportional to the light intensity. The quantum efficiency for the *trans*→*cis* change is in the neighbourhood of unity, while for the reverse change the efficiency is very low. In the *cis*-form slight decomposition into carbon dioxide and bromostyrene has been observed.

Physical measurements of the heat of formation, electrical moment, Raman spectra and photochemical activity indicate that the energy content of a *cis* molecule is relatively greater than the corresponding *trans*-form, and thus, there being no higher energy level which is stable, excitation by light either causes a decomposition of the *cis*-molecule or brings about a partial conversion into the *trans*-form by means of collisions of the second kind.



32. Studies on the dependence of optical rotatory power on chemical constitution. Part XVIII.—Stereoisomeric aminoanilino-, and aminodimethylanilino-, methylenecamphors and their derivatives.

BAWA KARTAR SINGH and BHUTNATH BHADURI, Cuttack.

Aminoanilinomethylenecamphors (*m* and *p*) have been prepared by hydrolysing the condensation products of aminoacetanilides (*m* and *p*) with oxymethylenecamphors (*d*, *l*, *dl*). *p*-Aminodimethylaniline has also been condensed with oxymethylenecamphor. The rotations of these compounds are, without exception, found to obey the simple dispersion law of Drude,

$$[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}.$$

In the investigations of the effect of constitution on the rotatory power, much difficulty is often met with if we confine the comparison to a particular wavelength. For the compounds which exhibit *simple* dispersion, we may overcome this difficulty by comparing the values of the *absolute* specific rotation of the compounds which are numerically equal to *k*'s of the Drude equation when

$$\lambda = \sqrt{\lambda_0^2 + 1}$$

(always in the infra-red region);  $\lambda_0$ 's being the absorption bands of the particular compounds.

From such a study we notice that the *polar* effect of a substituent group is traceable in the optical activity of these compounds. Substituent influence of the different groups in order of decreasing rotatory power is represented by,  $\text{NH}_2 > \text{N}(\text{CH}_3)_2 > \text{H} > \text{CH}_3 > \text{Cl} > \text{Br} > \text{I}$ , which agrees well, subject to minor variations, with the *polar* series as well as with the dissociation constant one of the substituted anilines, with which oxymethylenecamphor is condensed to get the present series of compounds.

The *solvent* and *position isomerism* effects on optical activity are also discussed.

33. Studies on the dependence of optical rotatory power on chemical constitution. Part XIX.—Stereoisomeric xylidinomethylenecamphors.

BAWA KARTAR SINGH and BHUTNATH BHADURI, Cuttack.

The optically active (*d* and *l*) xylidinomethylenecamphors (*m* and *p*) have identical rotation and are found to obey the *simple* dispersion law of Drude.

It was anticipated that the further introduction of any group (such as  $\text{CH}_3$ ) having a polarity similar to the one (in the present case,  $\text{CH}_3$ ) already in the nucleus, will supplement the effect of the latter; (in this case) will lower the rotation of the parent compound.

From a study of the values of the *absolute* specific rotation of the compounds, we get the following expected sequence of decreasing optical

rotatory power :  $\text{H} > \text{CH}_3 > \begin{matrix} \text{CH}_3 \\ < \\ \text{CH}_3 \end{matrix}$  which agrees exactly with the

specific inductive capacity series and the dissociation constant one of the condensed bases; and thus the analogy between the effect of substitution on optical activity and on other electrophysical properties to which attention has been already drawn by Betti, Perkin, Rule and ourselves in previous communications, is further experimentally confirmed.



34. Studies on the dependence of optical rotatory power on chemical constitution. Part XX.—The rotatory dispersion of stereoisomeric hydroxyphenylaminomethylenecamphors and their acetylated and benzoylated derivatives.

BAWA KARTAR SINGH and SAILESH CHANDRA SEN, Cuttack.

Amido-phenols (*o*, *m*, *p*) have been condensed with oxymethylene-camphors (*d*, *l*, *dl*). The rotatory dispersion of the optically active isomerides (*d*, *l*) are found to be identical and can be expressed by the simple dispersion equation of Drude,

$$[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}.$$

The replacement of a hydrogen atom by a negative group such as hydroxyl (OH) diminishes the rotation. The effect of substitution on optical activity is represented by the series which agrees subject to minor variations with the *polar* one. The acetylation and benzoylation of the OH group reduces the rotation of the parent compound. The influences of the solvent and of the position isomerism on the rotatory power are also discussed.

35. Studies in steric hindrance. Part II.—The isomerism of the monomethyl esters of 3-bromo-phthalic acid.

P. RAMASWAMI AYYAR, Bangalore.

The preparation of 3-bromo-phthalic acid in good yield from Naphthalene for the above purpose is under investigation as follows:—

(i) Naphthalene→. (ii) I-nitro-Naphthalene→. (iii) I-nitro-bromo-Naphthalene→. (iv) I-amino-bromo-Naphthalene→. (v) Bromo-phthalic acid.

The product in stage (iii) is found to be mainly I-nitro-5-bromo-Naphthalene along with a small quantity of I-nitro-8-bromo-compound.

The direct bromination of phthalic anhydride is also being studied for the same purpose.

Further work is similar to methods adopted in Part I (*Indian Science Congress*, 1932, *Chemistry Abstracts*, No. 144).

36. Some derivatives of nitroisobutylglycerin (2-nitro-2-methylol-propandiol-1.3) : I.—The trichloride and the tribromide.

KANTILAL CHHAGANLAL PANDYA, Agra.

Nitromethane, prepared by Steinkopf (Steinkopf, *Kirchhoff*, *Ber.* 1909, 42, 3439) and Wahl (*Bull. Soc. Chim.* 1909, [4], 5, 180), was condensed with formaldehyde, in the presence of potassium bicarbonate, as described by Henry (*Bull. Soc. Chim.* 3, 13, 1001). The nitroisobutylglycerin came out in crystals on keeping the reaction product in a vacuum desiccator. The nitro-alcohol was purified by recrystallisation and had all the characteristics described by Henry, including the m.p., which was 156-157°C. (Henry, 158°-159°).

Several methods were tried for the preparation of the trichloride, of which all failed except two. The first involved the use of phosphorus pentachloride, which, however, gave small yield. Thionyl chloride in the presence of pyridine (Darzens, *C. r.* 1911, 152, 1314) and with some special modifications gave a theoretical yield. The nitroisobutylglyceryltrichloride could be purified by sublimation or by recrystallisation from warm chloroform. It melted at 107°-108°C. Analysis confirmed its identity.

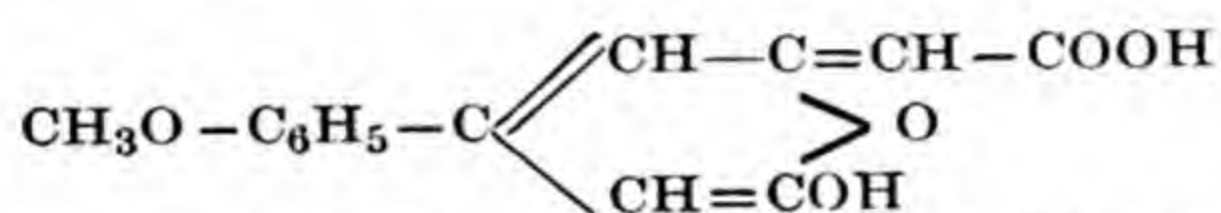


The tribromide was obtained in varying but small yields by means of phosphorus tribromide in a sealed tube as well as in a flask. On purifying it gave a m.p. 89°C. Whenever the reaction mixture was heated above a certain range, decomposition accompanied by flames and large volume of black smoke and lachrymetric fumes invariably took place. Analysis confirmed identity.

37. Action of acetic anhydride and sodium acetate on anhydrides of  $\beta$ -aryl-glutaconic acids: formation of  $\beta$ -aryl-glutaconyl-acetic acids.

D. B. LIMAYE and V. M. BHAVE, Poona.

The  $\beta$ (4-methoxy-phenyl)-glutaconic anhydride described by us in the *Journal of the Indian Chemical Society*, 1931, 8, 137, was treated with acetic anhydride and sodium acetate for acetylating the hydroxy group. However, instead of the expected neutral acetyl derivative the anhydride gave the enolic form of  $\beta$ (4-methoxy-phenyl) glutaconyl-acetic acid



melting at 132° (corresponding keto form melts at 180°), a reaction similar to the Gabriel's reaction for the preparation of phthalyl-acetic acid from phthalic anhydride and also not inconsistent with the hydroxy structure suggested by Thorpe for  $\beta$ -aryl-glutaconic anhydrides. This enolic acid (m.p. 132°) gave a strong coloration with Ferric chloride. On loss of one mol. of CO<sub>2</sub>, it gave the lactone  $\beta$ (4-methoxy-phenyl)-methylene-glutaconide (m.p. 112°).

This lactone as well as the original acid, on alkali treatment, gave  $\beta$ (4-methoxy-phenyl)- $\gamma$ -aceto-vinylacetic acid (m.p. 125°). This vinyl-acetic acid lost a mol. of CO<sub>2</sub> and gave 4-methoxy- $\alpha$ -methyl-benzylidene acetone, which on mild oxidation gave the known 4-methoxy- $\beta$ -methyl-cinnamic acid (m.p. 152°). Also on reduction with sodium amalgam, the above vinylacetic acid gave  $\beta$ (4-methoxy-phenyl)- $\gamma$ -aceto-butyric acid (m.p. 104°), a known compound.

The reaction was also extended to the anhydrides of (1)  $\beta$ (4-methoxy-3-methyl-phenyl), (2)  $\beta$ (2-methoxy-5-methyl-phenyl)-, (3)  $\beta$ (phenyl)-, (4)  $\beta$ (2-methoxy-4-methyl-phenyl)-, and (5)  $\beta$ (2-methoxy-phenyl)-glutaconic acids, with similar results.

38. Nitration. Part V.—Simultaneous nitration and oxidation of m- and p-xylenes.

P. S. VARMA and R. K. SOBTI, Benares.

Systematic investigation of the nitration of m- and p-xylenes has been made by using different nitrating agents under different conditions. It has been possible to get nitro-xylenes along with more or less quantity of nitro-toluic acids. The conditions under which the better yield of one or the other of the products is obtained have been studied to some extent.

39. Nitration. Part VI.—Nitration of benzene in presence of Bromine and Iodine.

P. S. VARMA and A. K. CHAKRAVARTY, Benares.

In a communication from this laboratory (Varma and Kulkarni, *Jour. Amer. Chem. Soc.*, XLVII, 1925, 143) it was stated that a trace of iodine catalytically favours the formation of di-nitro-benzene by the



action of a mixture of nitro-sulphonic and fuming nitric acids on benzene. It has been possible to investigate this problem further and find out if iodine or bromine has got any influence on the nitration of benzene. A number of experiments have been carried on which show that bromine and iodine increase the yield of nitro-benzene when the amount of sulphuric acid in the nitrating mixture does not fall below a certain limit. If the amount of sulphuric acid is less than a certain limit, bromine fails to affect the yield, whereas iodine decreases the yield of the nitro compound.

#### 40. Halogenation. Part XII.—Bromination of pseudo-cumene and para-cymene.

P. S. VARMA and D. N. SEN GUPTA, Benares.

An exhaustive study of the bromination of pseudo-cumene and para-cymene has been made. In the case of pseudo-cumene, mono-, di- and tri-nuclear substituted compounds are obtained in the dark. In the diffused daylight, nearly the same products are obtained as those in the dark. In direct sunlight, however, only side-chain substitution takes place. If the reaction is carried on a water bath, only mono substitution takes place, whereas if the reaction is carried on a paraffin bath at about the temperature of the boiling point of pseudo-cumene, di- and tri-derivatives are obtained. It is very interesting to observe that under the conditions in which only side-chain substitution takes place in the case of pseudo-cumene, if mono-bromo-pseudo-cumene is subjected to bromination, only nuclear substituted derivatives are obtained. Bromination has also been carried on in presence of a number of other substances, such as sulphuric acid (strong and fuming), nitric acid (strong and fuming), a mixture of sulphuric and nitric acids, and a mixture of nitro-sulphonic and fuming nitric acids. Fuming sulphuric acid gives a good yield of the nuclear substituted derivatives. The best yield of the nuclear substituted derivatives is, however, obtained by using a mixture of nitro-sulphonic and fuming nitric acids.

#### 41. Halogenation. Part XIII.—Bromination and iodination of benzo-nitrile.

P. S. VARMA and N. B. SEN GUPTA, Benares.

Bromination and iodination of benzo-nitrile have been studied more systematically as a result of which a number of bromo- and iodo-derivatives have been obtained. These derivatives have been obtained before by indirect methods only. In addition to these bromo- and iodo-derivatives, benzoic acid and benzamide are the other products obtained. Attempts have been made to find out the conditions under which the maximum yield of the halogen derivatives could be obtained.

#### 42. Halogenation. Part XIV.—Bromination of m-xylene.

P. S. VARMA and R. K. SOBTI, Benares.

Bromination of m-xylene in presence of halogen carriers, such as iron, aluminium, iodine, sulphur, selenium, aluminium chloride, and iron chloride, in (1) direct sunlight, (2) diffused daylight, and in (3) dark, has been studied. The products obtained are, to some extent, different under the latter conditions. In the case of direct sunlight and diffused daylight, both the nuclear as well as the side-chain substitution takes place, whereas in the dark only the nuclear substitution takes place. It has been possible to find out the conditions that would give the maximum yield of the nuclear or the side-chain derivatives.



43. Halogenation. Part XV.—Chlorination of benzene in presence of halogen carriers and sunlight.

P. S. VARMA and A. K. CHAKRAVARTY, Benares.

A number of experiments have been carried on in which benzene and chlorine have been kept for different lengths of time in contact with a number of substances, such as pyridine, aluminium-mercury couple, aluminium powder, ferric oxide, iodine, antimony, etc., in the dark, or in diffused daylight or in direct sunlight. Very little action takes place in the dark. Some action takes place in the diffused daylight, but the action in direct sunlight is very prominent. Both addition and substitution derivatives in very good yields have been obtained. Different halogen carriers have different effect on the yield of the addition and substitution derivatives. Some halogen carriers, however, have no action at all.

44. Halogenation. Part XVI.—Bromination and iodination of ethyl benzene.

P. S. VARMA and B. RAMSUBRAMANYAM, Benares.

Bromination and iodination of ethyl benzene have been studied in the dark, in diffused daylight and in direct sunlight in the presence or the absence of halogen carriers. In the dark only nuclear substitution takes place, whereas in the diffused daylight or direct sunlight both nuclear as well as side-chain substitution takes place. By carrying on a number of experiments, it has been possible to find out the conditions, including the nature of the halogen carriers, that will give the best yield of the nuclear or the side-chain substitution derivatives.

45. Halogenation. Part XVII.—Iodination of phenanthrene.

P. S. VARMA and P. V. VISHWANATHAN, Benares.

By the study of the action of iodine on phenanthrene under different conditions, it has been possible to prepare three definite iodo-derivatives of phenanthrene. The physical as well as the chemical characteristics of these compounds have been studied. Since there is no mention of any iodo-derivative of phenanthrene in the literature, attempts are being made to find out the position of the iodine atom or atoms in the compounds obtained.

46. Derivatives of salicylic acid. Part I.

R. L. ALIMCHANDANI, N. M. SHAH, and P. K. NAVALGUND, Dharwar.

Chattaway and Calvet (*J.C.S.*, 1928, 1090) tried the reaction of salicylic acid and chloral in presence of sulphuric acid: the product was found to be a complex mixture of substances which could not be crystallised. The present authors, thinking that this complexity may be due to the free hydroxyl group taking part in the reaction, have condensed chloral with the methyl ether of salicylic acid and have isolated a crystalline product which contains the group  $-\text{CH}(\text{OH})\text{CCl}_3$ , the chloral molecule attacking either *ortho* or *para* position to the  $-\text{OMe}$  group. On reduction with zinc and acetic acid, the group  $-\text{CH}(\text{OH})\text{CCl}_3$  changes to  $-\text{CH}_2\text{CHCl}_2$ . (Meldrum and Alimchandani, *J. Ind. Chem. Soc.*, 1925, 2, 1-9.) Further work is in progress.



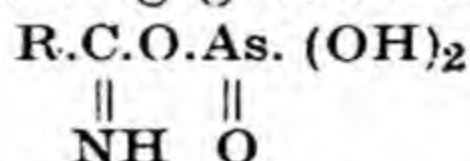
47. A study in the preparation and the properties of Organo-arsenicals by means of arsenic acid.

K. G. NAIK and K. N. CHOKSHI, Baroda.

The action of arsenic acid has been studied with the following acid amides :—

(1) Formamide, (2) acetamide, (3) chloracetamide, (4) cyanacetamide, (5) propionamide, (6) lactamide, (7) butyramide, (8) isobutyramide, (9) valeramide, (10) isovaleramide, (11) malonamide, (12) carbamide, (13) thiocarbamide, (14) carbanilide, (15) thiocarbanilide.

The above amides, when fused with arsenic acid, reacted to give the imino-ethers of the following general constitution :—



These substances are highly soluble in water and can be crystallised from it in the form of large colourless perfectly pure crystals. Boiling with concentrated hydrochloric acid does not decompose them. Hydrogen sulphide decomposes the above compounds giving rise to arsenic sulphide. Sulphur dioxide and sodium bisulphite react with these compounds giving rise to a mixture of trioxide and pentoxide of arsenic. Alkali hydroxides decompose the above compounds with the evolution of ammonia, indicating the separation of the acid amides.

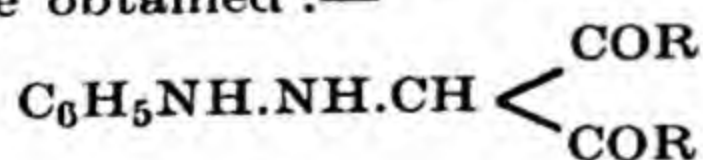
48. A study of the labile nature of the bromine atoms substituted in the reactive methylene —CH<sub>2</sub> group, and the effect of the negative character of the adjoining carbonyl groups, using phenyl hydrazine as the reagent.

K. G. NAIK and K. N. CHOKSHI, Baroda.

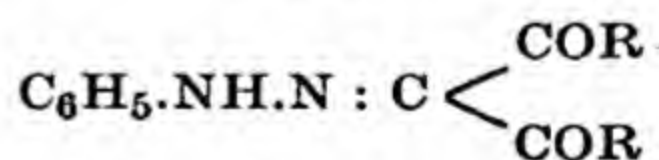
The reaction of phenylhydrazine was studied with the following compounds :—

(1) Monobromomalonamide, (2) dibromomalonamide, (3) monobromomalon-p-bromoanilide, (4) dibromomalon-p-bromoanilide, (5) dibromomalon-2 : 4-dibromoanilide, (6) monobromomalon-p-toluidide, (7) dibromomalon-p-toluidide, (8) dibromomalon-2 bromo-p-toluidide, (9) monobromomalon-4-bromo-o-toluidide, and (10) dibromomalon-4-bromo-o-toluidide.

When the above compounds were refluxed with phenylhydrazine in presence of alcohol, compounds of the following general constitution were obtained :—



I



II

Summarising the results obtained herein, it was found that the labile nature of the bromine atoms of the methylene group in the bromo-derivatives of the amide and the substituted amides of malonic acid, increases with total increase in the negative character of the adjoining carbonyl groups, attached to the central reactive methylene group. It was also found that in the case of the dibromo derivatives, one of the bromine atoms is more reactive than the other.

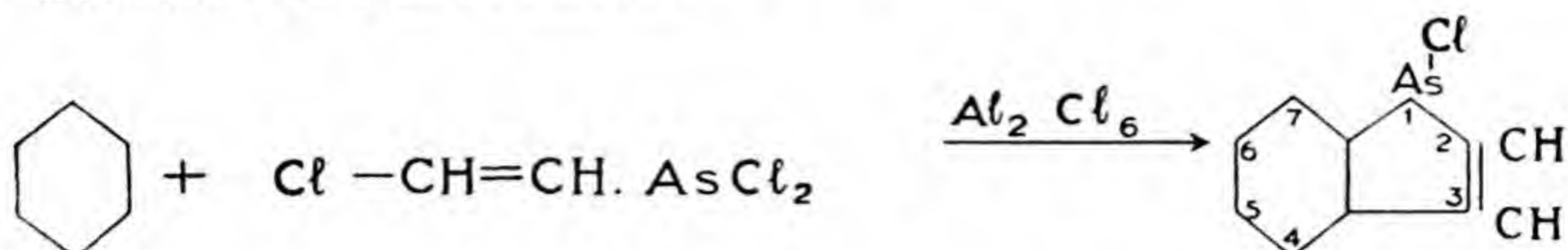
Since the labile nature of the bromine atoms in the substituted methylene group is directly proportional to the reactivity of the hydrogen atoms of a reactive methylene group in compounds containing the grouping —CO.CH<sub>2</sub>.CO—, the above conclusions are quite in a line with the views put forward from time to time since these investigations were undertaken in these laboratories.



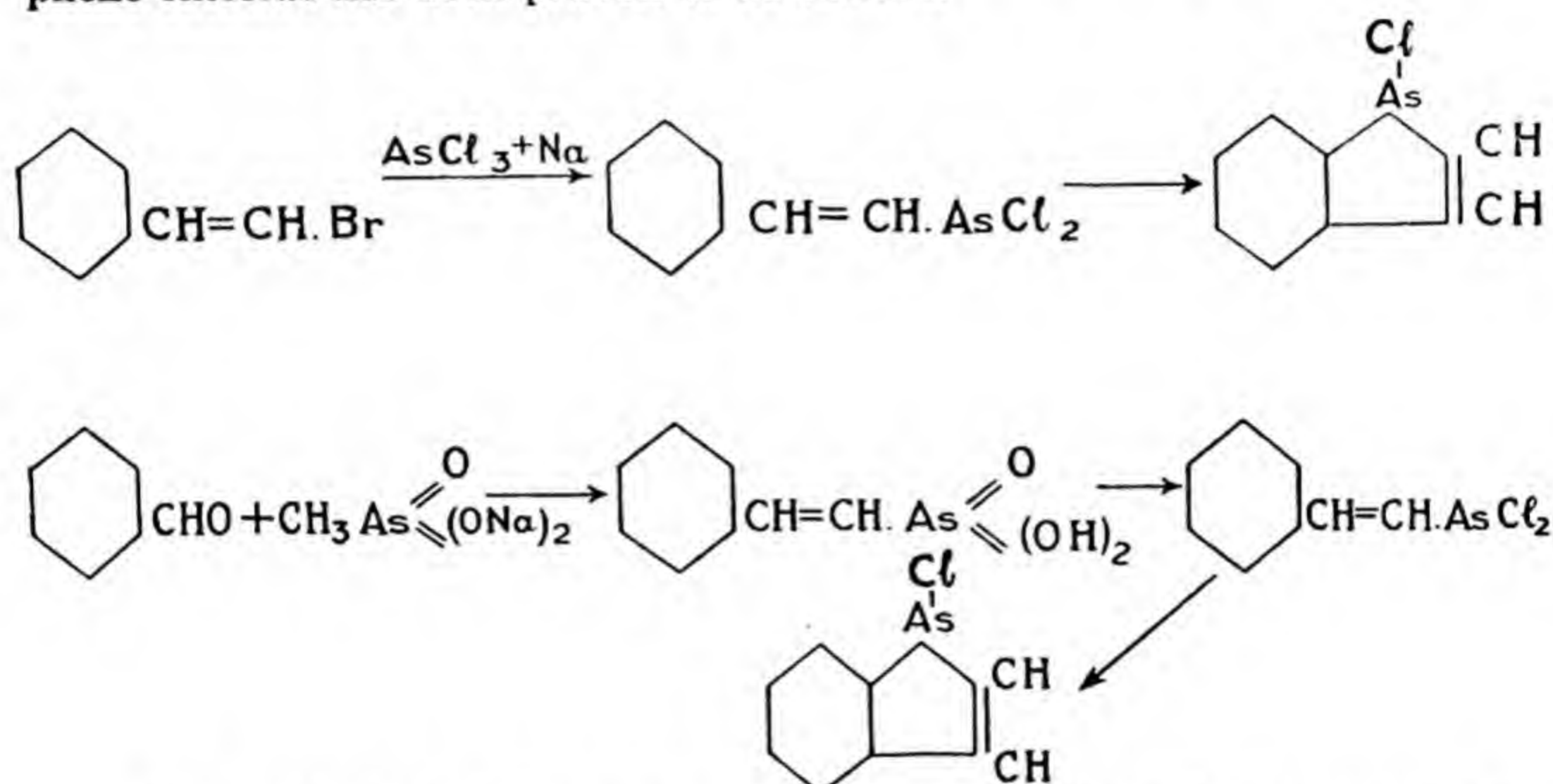
## 49. Studies in organo arsenic compounds.

H. N. DAS GUPTA, Calcutta.

The synthesis of Benzarsenophene chloride has been effected by the action of  $\beta$ -chloro-vinyl-dichloro-arsine on benzene in presence of anhydrous aluminium chloride as follows:—



The following scheme shows how the formula given to Benzarsenophene chloride has been proved to be correct.



The oxidation of Benzarsenophene chloride gives the corresponding arsinic acid derivative. The arsinic acid, on treatment with nitric acid (sp. gr. 1.5), gives the nitro-arsinic acid.

Attempts to prepare the Benzarsenophene via ortho-amino-cinnamic acid by preparing the arsinic acid derivative and then applying Fischer's method of synthesis of Indole proved futile due to the formations of tertiary arsinic oxides at the outset. (cf. *Journal Indian Chem. Soc.*, 417, 1931.)

Further work with other derivatives of the Benzarsenophene chloride are in progress.

## 50. Detection of aldehydes and ketones by colorimetric tests.

M. N. GOSWAMI, H. N. DAS GUPTA, and B. K. MUKHERJI, Calcutta.

The yellowish brown colour of the solution of picric acid and N/10 aqueous caustic soda is discharged by aldehydes and ketones having no adjacent  $-\text{CH}_2$  group; while those containing the said grouping impart an intense red coloration.

The red colour developed by the addition of aqueous N/50 caustic soda to a solution of ortho- or meta-nitrophenol in alcohol is discharged



only by the aldehydes (both aliphatic and aromatic) and not by the ketones. Under the same condition, the yellow colour of para-nitrophenol with alkali is not affected either by the aldehydes or the ketones.

51. Preparations of sulphoarsinic acids of coumarins.

M. N. GOSWAMI and H. N. DAS GUPTA, Calcutta.

6-amino and 7-methyl-6-amino coumarins have been sulphonated by fuming sulphuric acid; the sodium salt by Bart's reaction gave the corresponding mono sulphoarsinic acids. The position of the sulphonic acid group is most probably in the benzene ring. Further work in this direction is in progress.

52. A new method of synthesising benzopyrylium compounds.

M. N. GOSWAMI and A. K. CHAKRAVORTY, Calcutta.

The compound prepared from coumarin and resorcin with  $\text{POCl}_3$  as condensing agent (*vide Proceedings, Science Congress, 1932*) has now been definitely shown to be 3': 5'-dihydroxy benzo pyrylium chloride. The identity of the di-methoxy derivative (m.p.  $175^\circ$ ), prepared from coumarin and dimethyl resorcin with  $\text{POCl}_3$ , with the compound (m.p.  $175^\circ$ ) synthesised from salicylaldehyde and dimethyl resacetophenone via Robinson's method has been established. Other pyrylium compounds by the new method are being prepared.

53. Morellin.

N. C. KELKAR and B. S. RAO, Bangalore.

A methoxy derivative of morellin has been obtained (m.p. 156). The methoxy derivative, on oxidation with alkaline permanganate, yields an acid which is being investigated.

54. Turmerol.

B. S. RAO, Bangalore.

An alcohol  $\text{C}_{15}\text{H}_{22}\text{O}$  has been synthesised from curcumone and has the following constants: b.p. 143–145/6 mm.,  $d_{30}^{30}$  0.9504,  $n_D^{30}$  1.5062

(natural turmerol has b.p. 145–150/6,  $d_{30}^{30}$  0.9521,  $n_D^{30}$  1.5115). The synthetic product gives on oxidation with permanganate an acid identical with that from natural turmerol.

55. The reactivity of dimethyldihydroresorcin. Part III.—  
Formation of azo dyes.

B. H. IYER and G. C. CHAKRAVARTI, Bangalore.

Dimethyldihydroresorcin behaves as a phenol towards diazotised amines and yields azo compounds of the usual type from a finally acid medium. Azo derivatives of the following amines are described, aniline, o-, m- and p-toluidines and  $\alpha$ - and  $\beta$ -naphthyl amines. These dyes are either bright yellow or orange in colour.

From an alkaline medium in some cases, deep-red substances insoluble in alkali are obtained. They may be either o-azo compounds or oxydiazoles. Coupling with aminosulphonic acids is also being tried with a view to prepare some water soluble dyes.



56. Reactivity of dimethyldihydroresorcin. Part IV.—  
Formation of benzylidene derivatives.

GOPAL V. NEVGI and G. C. CHAKRAVARTI, Bangalore.

Substances, containing reactive methylene groups, condense with free or substituted benzaldehydes to give benzhydrol or benzylidene derivatives. Peculiarly enough, under similar conditions dimethyl-dihydroresorcin condenses with aldehydes to give compounds of the triphenylmethane or phenylxanthene series (*J. Indian Inst. Sci.*, 1931, p. 141). By careful modification of the experimental conditions as well as by the hydrolysis of the triphenyl methane compound we have been able to obtain products in which equimolecular proportions of the reacting substances have taken part. Only the nitro-substituted compounds behave as mentioned above.

57. Reactivity of dimethyldihydroresorcin. Part V.—  
Synthesis of a reduced pyridine derivative.

GOPAL V. NEVGI and G. C. CHAKRAVARTI, Bangalore.

Salicylaldehyde combines with dimethyldihydroresorcin giving o-hydroxy-benzaldimethyl-dihydroresorcin anhydride (1). Attempts to prepare the corresponding nitrogen analogue from o-aminobenzaldehyde led to the formation of 1-keto-3-dimethyl-tetrahydroacridine. The reduction of 2:7-tetramethyl-4:5-diketo-o-nitrophenyloctahydroxanthene also did not yield the desired compound (Iyer and Chakravarti, *J. Indian Inst. Sci.*, 1931, p. 157). The direct replacement, however, of the oxygen of the ring in (1), by nitrogen, by means of aqueous alcoholic ammonia, has given a product, the constitution of which is under investigation.

58. Synthesis of phenylthioxanthenes.

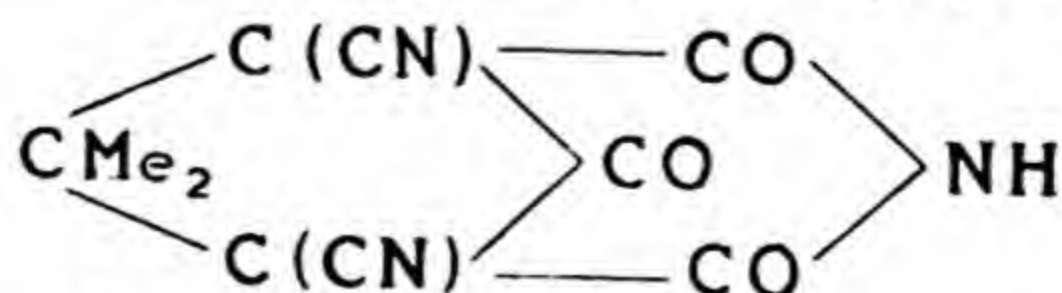
GOPAL V. NEVGI and G. C. CHAKRAVARTI, Bangalore.

In continuation of the work on the synthesis of phenyl-thioxanthenes (*vide Indian Science Congress Abstracts, Section of Chemistry*, 1932), it has been observed that, under the conditions of the reaction, oxygen derivatives of the substituted phenyl-thio-xanthenes were formed, invariably in the cases of sulphides in which the methoxy group is in the meta-position to the sulphur atom. Moreover during attempts to convert the methoxy groups into the hydroxy ones it has been observed that the former are replaced by hydrogen.

59. Studies in bridge-formation. Part I.

R. C. DAS GUPTA and P. C. GUHA, Bangalore.

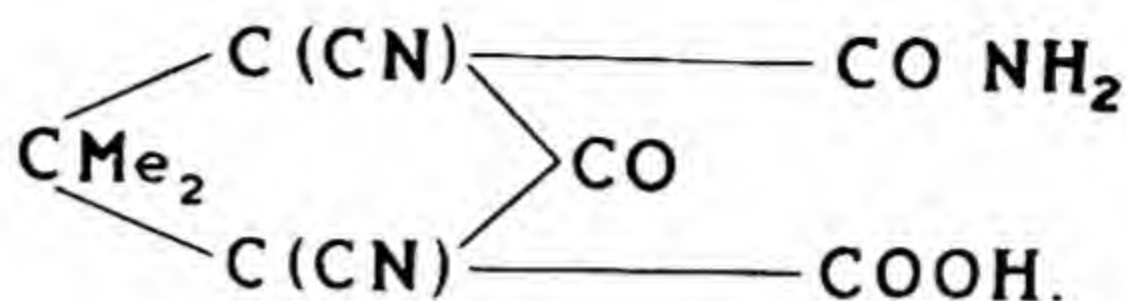
By reacting the disodium derivative of Guareschimide with carbonylbromide two compounds have been isolated, the first one (m.p. 200°C.) of the following constitution and a second one (m.p. 233°C.) which from



the experimental evidence so far available is supposed to possess a bridged structure and is under further investigation. When the latter compound is boiled for a long time with water, a compound crystallises out and melts at 155°C.



The action of Phosgene on the sodium derivative of Guareschimide yields a very small quantity of a substance (m.p. 170°C.) which possesses the structure.



#### 60. Attempted synthesis of cantharic acid II.

V. N. PAI and P. C. GUHA, Bangalore.

Methylation of methyl cyclohexan-1.4-dione-2.3-dicarboxylate (*Indian Science Congress Abstracts*, 1932, *Section of Chemistry*, 34) was tried using sodium methoxide in alcohol and benzene suspension under various experimental conditions. In all cases, the 2-C-methyl derivative and the dimethyl ether of methyl-4.5-dihydro-3.6-dihydroxy-phthalate were formed in varying proportions. The products of the interaction of the diketo-diester and methyl iodide in presence of sodamide in benzene suspension are under investigation.

#### 61. Attempts towards synthesis of cantharidin.

B. H. IYER and P. C. GUHA, Bangalore.

The reaction between the disodium derivative of diacetyl-diethyl-adipate and dibromo-succinic ester (*Indian Science Congress Abstracts*, 1932, *Section of Chemistry*, No. 123) failed to give compounds having vesicant properties. Preparation of symmetrical dimethyl-dichloro-succinic acid having presented many difficulties, condensation of this with the disodium derivative of diacetyl-diethyl-adipate has been postponed.

Present attempts are progressing in the following lines. The sodium derivative of malonic ester is allowed to react with succinyl chloride. Succinyl dimalonester thus formed is separated from the accompanying succinyl malonester by preparing the disodium derivative of the former. This has been methylated using methyl iodide, but the yield is not satisfactory. Hence the sodium derivative of methyl malonic ester is being reacted with succinyl chloride to prepare 2 : 5-diketo-1 : 6-dimethyl suberate which on ring closure in positions 1 and 6 is expected to give 2 : 5-diketo-cantharidic acid.

#### 62. Endo-thio triazoles and thiobiazoles.

S. L. JANNIAH and P. C. GUHA, Bangalore.

In continuation of the work reported last year, paper No. 192 of the *Section of Chemistry*, the following facts have been observed :—

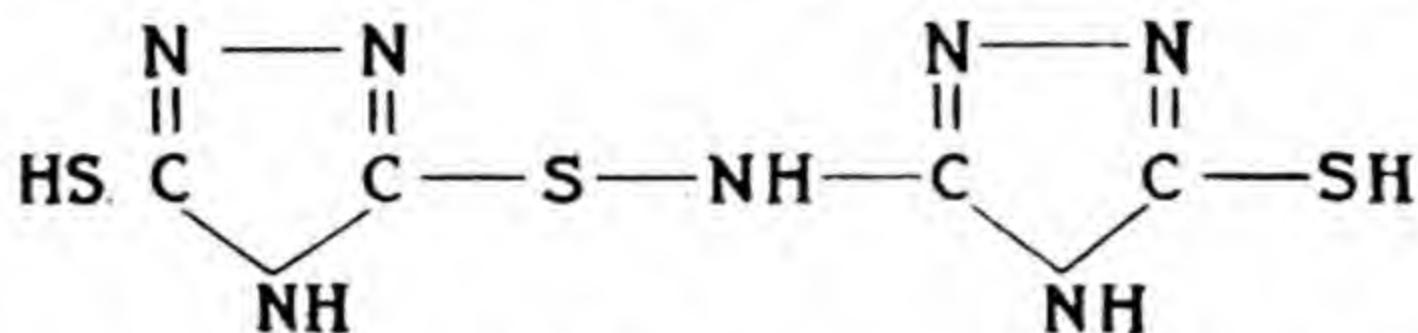
3 : 5-dithio-triazole, on treatment with acetic anhydride and subsequent hydrolysis of the acetyl derivative, gave 3 : 5-endothio-3-thiol-1 : 2 : 4-triazole. But in the case of 3 : 5-dithio-4-N. phenyl-1 : 2 : 4-triazole interesting results have been obtained, viz. an interchange of positions between the S-atom and the NPh-group. Actually 3-thio-5-N. phenyl-1 : 2 : 4-thiobiazole was obtained by treating the above-mentioned triazole with concentrated hydrochloric acid, as also the endo-compound 3 : 5-endothio-5-phenylimino-1 : 2 : 4-thiobiazole. No such interchange of positions occurred with 3 : 5-dithio-1-phenyl-1 : 2 : 4-thiobiazole.



## 63. Action of hydrazine hydrate on persulphocyanic acid.

D. R. MEHTA and P. C. GUHA, Bangalore.

From does not give any detail about his experiments regarding the action of hydrazine hydrate upon persulphocyanic acid though he describes the isolation of two compounds, viz. hydrazine salt of 3 : 5-dithiol-1 : 2 : 4-triazole and 3 : 5-amino : thiol-1 : 2 : 4-triazole. As the result of about 15 experiments with varying quantities of hydrazine hydrate of different strength upon varying quantities of persulphocyanic acid under different experimental conditions, it has now been possible to find out the best method of preparation of both of his compounds as also a third compound melting at 252-53° which from its analytical value, molecular weight, acetyl and benzyl derivatives appears to be



Another new compound isolated in this reaction melts at 185-187° with frothing and gives the compound melting at 252-53° on being heated at 200° for two hours.

## 64. Ring closure of hydrazodithiodicarbonamides.

D. R. MEHTA and P. C. GUHA, Bangalore.

The action of hydrochloric acid (d, 1.19), acetic anhydride and simple heat upon monophenyl, monotolyl, monoxyl, and the corresponding disubstituted derivatives of hydrazodithio-dicarbonamides ( $\text{RNH-CS-NH-NH-CS-NH}_2$ ,  $\text{RNH-CS-NH-NH-CS-NHR}$ ) has been studied and a number of interesting thiobiazoles and triazole derivatives isolated. Several of the isolated products appear to be isomeric (endo ?) with some of the compounds of this series already known.

## 65. Reactions of dinitriles with aromatic hydroxyaldehydes.

N. PALIT, Patna.

Simple aliphatic and aromatic aldehydes have been found to react with dinitriles (imido-acyl-methyl-cyanides) to form 3 : 5 dicyano-pyridine derivatives from one molecule of the aldehyde and two molecules of the dinitrile with the elimination of a molecule each of water and ammonia (E. V. Meyer, *J. Pr. Chem.*, 39, 262-83 ; *Chem. Zentr.*, 1908, 591-94). In the present investigation aromatic hydroxyaldehydes were employed to see if the presence of the additional hydroxyl group modify the above general course. It was expected with the ortho compound that the dinitrile might also react in the tautomeric amido form in which case one molecule of each would react to give 3-cyanoquinoline derivatives in the same way as o-aminobenzaldehyde and ortho amino-acetophenone react with it. It was found, however, that the reaction did not go in this way at all. The general course of the formation of 3 : 5 dicyano-pyridines was reproduced in most cases while with salicylaldehyde the principal reaction undertook an entirely different course (Mohr, *J. Pr. Chem.*, 1897, 124). In this case, curiously enough, two molecules of the aldehyde reacted with one molecule of the dinitrile with the elimination of two molecules of water. The crystalline product is insoluble in alkali, stable

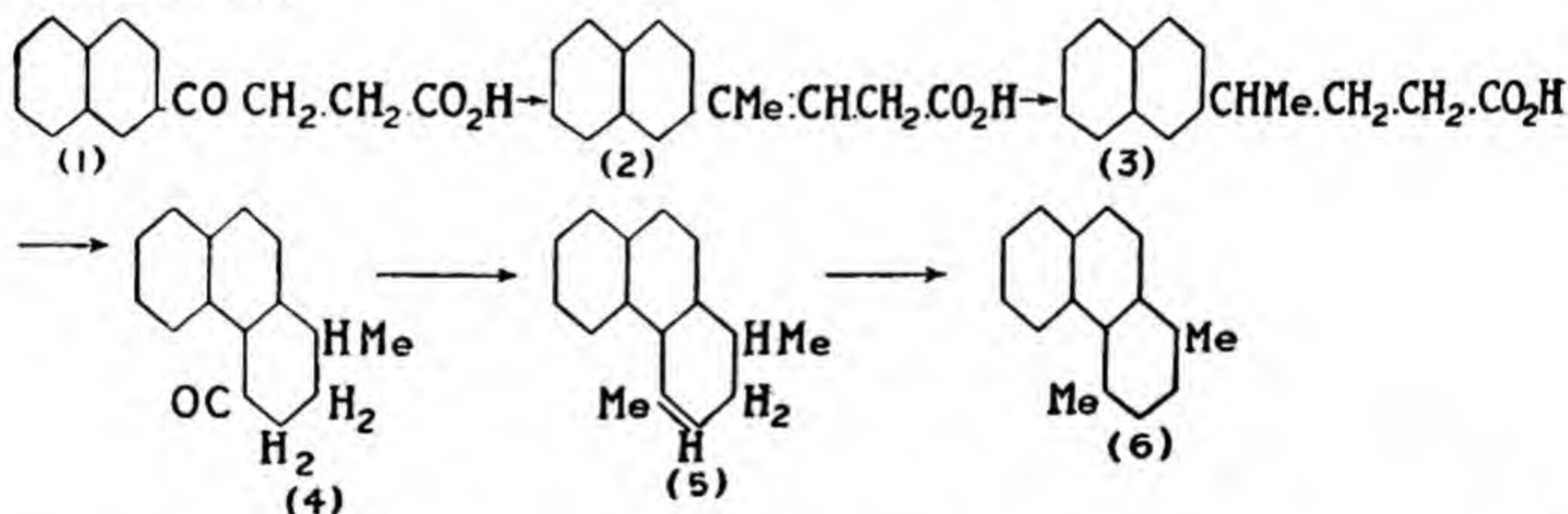


towards hydrochloric acid and has no aldehyde group. It forms a mono-acetyl derivative very easily and a trioxyderivative is obtained on hydrolysis with HCl under pressure. The author has reasons to believe that it is a xanthoquinoline derivative. Further work is in progress to elucidate its composition.

## 66. Synthesis of 1:4-dimethyl-phenanthrene.

S. C. SEN GUPTA, Calcutta.

$\beta$ -2-Naphthoyl-propionic acid (1) is prepared from naphthalene and succinic anhydride in presence of aluminium chloride (*J.C.S.*, 1932, 1128), the methyl ester (b.p.  $215^{\circ}/7\text{mm.}$ , m.p.  $74-75^{\circ}$ ) of the acid (1) is treated with methyl-magnesium iodide giving the unsaturated acid  $\lambda$ -(2 naphthyl)- $\Delta\beta$ -pentenoic acid (2) (m.p.  $131-133^{\circ}$ ). This unsaturated acid was reduced with hydriodic acid ( $d$  1.7) and red phosphorus giving the saturated acid (3), which on treatment with sulphuric acid gives 4-keto-1-methyl-1:2:3:4-tetrahydro-phenanthrene (4) (b.p.  $165-170^{\circ}/6\text{mm.}$ , semi-carbazone m.p.  $203-204^{\circ}$ ). This was next treated with methyl-magnesium iodide and the product (5) on dehydrogenation with selenium at  $300^{\circ}-340^{\circ}$  gives 1:4 dimethyl-phenanthrene (6) (m.p.  $77^{\circ}$ ). The picrate melts at  $155^{\circ}$ .

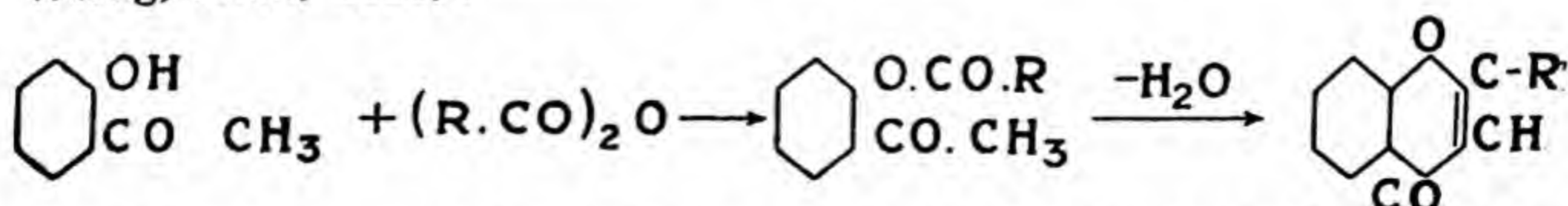


## 67. Studies in the Robinson reaction for the synthesis of chromones.

T. C. CHADDHA and K. VENKATARAMAN, Lahore.

Having studied the application of the Robinson method for the synthesis of chromones to gallacetophenone, 1-acetyl-2-naphthol, 2-acetyl-1-naphthol and 4:6-diacetylresorcinol (*J. Chem. Soc.*, 1929, 1931, 1932), the reaction has now been extended to *o*-hydroxyacetophenone, 2:5-dihydroxyacetophenone and 2:4:5-trihydroxyacetophenone. The colour reactions and dyeing properties of the new polyhydroxy-flavones thus prepared are recorded.

Attention has also been directed to the mechanism of the reaction. It has usually been assumed to proceed in two stages as follows (cf., Wittig, *Ann.*, 1924):



We have attempted the ring closure of the acetate and the benzoate of 2-acetyl-1-naphthol and of the acetate of 2-phenylacetyl-1-naphthol by means of each of the following reagents: the corresponding sodium salts, zinc chloride, phosphorus pentoxide in xylene, acetic anhydride,



and phosphorus oxychloride in chloroform. In no case could a chromone be isolated.

Contrary to Wittig (*loc. cit.*), the action of acid anhydrides on  $\omega$ -bromo-ketones (such as  $\omega$ -chlorogallacetophenone and 2-bromacetyl-1-naphthol) has not led to chromonols.

#### 68. A synthesis of 4-styrylcoumarins.

H. S. MAHAL and K. VENKATARAMAN, Lahore.

4-Styrylcoumarins have been made by treatment of o-hydroxy-phenyl styryl ketones (o-hydroxychalkones) with sodium phenylacetate and acetic anhydride. The following 4-styrylcoumarins were thus prepared: 3-phenyl-1-4-styrylcoumarin, 3-phenyl-4'-methoxy-4-styrylcoumarin, 3-phenyl-3' : 4'-methylenedioxy-4-styrylcoumarin, 3-phenyl-7 : 8 : 4'-trimethoxy-4-styrylcoumarin, 3-phenyl-7 : 8-dimethoxy-3' : 4'-methylenedioxy-4-styrylcoumarin, 3-phenyl-4-styryl-1 : 2- $\alpha$ -naphthapyrone, 3-phenyl-4'-methoxy-4-styryl-1 : 2- $\alpha$ -naphthapyrone and 3-phenyl-3' : 4'-methylenedioxy-4-styryl-1 : 2- $\alpha$ -naphthapyrone. 4-Styrylcoumarins unsubstituted in the 3-position could not be prepared by this method, the action of acetic anhydride and sodium acetate on o-hydroxychalkones leading only to the acetyl derivatives. 4-Styrylcoumarins have previously been made by Dey and Row (*J. Ind. Chem. Soc.*, 1924) by condensing coumaryl-4-acetic acids with aldehydes.

#### 69. 2-Styrylchromones.

K. C. GULATI, S. R. SETH, and K. VENKATARAMAN, Lahore.

In extension of previous work (Cheema, Gulati and Venkataraman, *J. Chem. Soc.*, 1932) and with the object of elucidating the constitution of pratensol and fukugetin, the synthesis of styrylchromones derived from resacetophenone and phloracetophenone has been undertaken. On account of the difficulties attending the demethylation of styrylchromones, hydroxyl groups were initially protected by benzylation. Benzylation of resacetophenone under prescribed conditions yielded *resacetophenone 4-benzyl ether*, which was treated with ethyl acetate and sodium. Ring closure was effected in the usual manner and the 7-benzyloxy-2-methylchromone was then condensed with benzaldehyde and p-benzyloxybenzaldehyde respectively. Debenzylation with acetic and hydrochloric acids led to 7-hydroxy-2-styrylchromone and 7 : 4'-dihydroxy-2-styrylchromone. Similar work on derivatives of phloracetophenone is in progress.

#### 70. An attempted new synthesis of oxy-protoberberine and a synthesis of 3-methoxy-oxy-protoberberine,

S. N. CHAKRAVARTI and A. P. MADHAVAN NAIR, Chidambaram.

Phthalide-carboxylic acid-chloride was condensed with  $\beta$ -phenylethylamine, when phthalide-carboxy- $\beta$ -phenylethylamide (m.p. 155°) was formed. Attempts to convert the amide into oxyprotoberberine were unsuccessful. With phosphorus pentachloride as the cyclising agent a crystalline substance (m.p. 153°) was obtained.

The acid chloride of Phthalide-carboxylic acid readily condensed with  $\beta$ -m-methoxy-phenylethylamine, giving phthalide-carboxy- $\beta$ -m-methoxy-phenylethylamide (m.p. 105°). When this was heated with phosphorus oxychloride and the product decomposed with ice, a basic substance separated, which on reduction with Zinc dust and acetic acid, converted into 3-methoxy-oxyprotoberberine (m.p. 143°).



71. A new synthesis of 3:10-dimethoxy-tetrahydroprotoberberine.

S. N. CHAKRAVARTI, N. A. VAIDYANATHAN, and A. VENKATASUBBAN, Chidambaram.

$\beta$ -m-methoxy-phenylethylamine and p-methoxy-phenyl-acetic acid, prepared by improved methods, were condensed together. P-methoxy-phenyl-aceto- $\beta$ -m-methoxy-phenyl-ethylamide (m.p.  $85^{\circ}$ ), thus obtained, was converted in a yield of more than 80% into 6-methoxy-1 (4'-methoxy-benzyl) 3 : 4-dihydro-isoquinoline. The base readily forms a hydrochloride and a picrate, and oxidizes readily on exposure to air and is readily reduced to 6-methoxy-1 (4'-methoxy-benzyl)-1 : 2 : 3 : 4-tetrahydro-isoquinoline, a base yielding a crystalline sulphate and picrate. The base was converted into N-formyl derivative, and the latter converted into 3 : 10-dimethoxy-dihydroprotoberberine, in a yield of about 20%, which was reduced to 3 : 10-dimethoxy-tetrahydroprotoberberine (m.p.  $139^{\circ}$ ).

72. Oxazine dye derived from 7-oxy-quinoline.

R. N. SEN and G. MUKHERJEE, Calcutta.

7-oxy-quinoline, which is analogous to  $\beta$ -naphthol, condenses with p-nitroso-dimethyl-aniline hydrochloride in absolute alcoholic solution in presence of zinc chloride and fuming hydrochloric acid on the water bath producing a violet dye analogous to Meldola's Blue.

73. Azo-triphenyl-methane and azo-pyronine dyes (ortho-series).

R. N. SEN and S. N. ROY, Calcutta.

Ortho-azo-aldehydes, prepared for the first time by coupling m-hydroxy-benzaldehyde with diazotised anilines, e.g. P-toluidine, o-, m-, and p-nitranilines and  $\alpha$ -naphthyl-amine, have offered an opportunity of studying the azo-triphenyl-methane and azo-pyronine dyes, containing the azo and the triphenyl-carbinol chromophores in the ortho-positions, and of comparing the effect of the two chromophores in the ortho-positions with their effect in the para-positions (Green and Sen, *J.C.S.*, 1912, 101, 1113; Sen and Sett, *J.A.C.S.*, 1924, 46, 111; Dutta, *J.C.S.*, 1926, 129, 1171) and in the meta-positions (Sen and Ghosh, *J.I.C.S.*, 1928, 5, 487; Dutt, *J.C.S.*, 1926, 129, 1171).

From a study of the various azo-triphenyl-methane dyes (prepared by condensing the aldehydes with dimethylaniline and o-cresotinic acid) and the azo-pyronine dyes (prepared by condensing the aldehydes with resorcinol, pyrogallol and diethyl-m-amino-phenol) it has been observed that the introduction of an azo-group in the ortho-position to the central carbon atom, is generally attended with an increase in the depth of colour, much less than in the case of p-compounds and almost similar to that of the m-compounds.

A marked difference between the azo-triphenyl methane dyes of the para- and the ortho-series is that the yellow shade on wool produced by the leuco-o-cresotinic acid compound of the p-series changes from yellow through maroon to dark green and black by after-chroming and the carbinols are remarkably polygenetic (Green and Sen, *loc. cit.*), but the yellow shade produced by the corresponding leuco-compounds in ortho-series changes only to dirty-brown on similar treatment, and the carbinols are only feebly polygenetic; and in these respects they are more akin to the corresponding compounds of the m-series (Sen and Ghosh, *loc. cit.*).



## 74. Dyes derived from Acenaphthenequinone. Part IV.

S. K. GUHA, Patna.

Extending the work of Sircar and Guha (*J. Chem. Soc.*, 1924, 125, 335), Guha (*J. Chem. Soc.*, 1931, 582) and Guha (Part III.—in course of publication in *J. Ind. Chem. Soc.*, 1932), the author with a view to study the tinctorial properties of azines having acenaphthene nucleus on both sides of the azine ring prepared Acenaphtha-, acenaphtha-3-chloro-, acenaphtha-3-bromo-, Acenaphtha-3 : 4-dinitro-acenaphthazine. Studies in their properties have been undertaken.

## 75. Dyes derived from Isatin.

S. K. GUHA and H. P. BASU MULLICK, Patna.

In view of the interesting tinctorial properties of acenaphtha-phenazines containing a 'NO<sub>2</sub>' group in the benzenoid part of the molecule and that of acenaphtha-acenaphthazine and its derivatives (*loc. cit.*) work has been undertaken to prepare similar azines in the isatin series. The compounds obtained up till now are 4'-nitro-, 5 : 4'-dinitro-, 5 : 7 : 4'-trinitro-, 5 : 7-dinitro-indophenazine, acenaphtha-, acenaphtha-5 : 7-dinitro-indazines. Work in this line is in progress.

## 76. Substantive cotton dyes from fluorenone.

A. C. SIRCAR and K. C. BHATTACHARYYA, Calcutta.

The paper deals with the preparation and properties of substantive cotton dyes obtained by coupling tetrazotised 2 : 7-diamino-fluorenone with various phenols and amines, such as phenol, resorcinol, salicylic acid,  $\beta$ -naphthol, 2-hydroxy-3-naphtholic acid, 1-naphthylamine-4-sulphonic acid, 1-naphthol-4-sulphonic acid, R-acid, G-acid, Cleve's acid, Lawrant's acid, H-acid, Y-acid, Schaffer's acid, and chromotropic acid.

## 77. Dyes derived from phenanthraquinone : Acenaphtheno-phenanthrazines.

P. C. DUTTA, Muzaffarpur.

It has been shown by Dutta, Prasad, and De (*J. Indian Chem. Soc.*, 1932, 9, 211) that the colour of the monoazinedyes, Phenanthraphenazines (Watson and Dutta, *J.C.S.*, 1921, 119, 1211) and Phenanthranaphthazines (Sircar and Dutt, *J.C.S.*, 1922, 121, 1944) is deepened to a certain extent with the increase in the complexity of the molecule. The present investigation was undertaken with a view to study further the above observation and it deals with azine dyes obtained by condensing various phenanthraquinone derivatives with 4 : 5-diaminoacenaphthene (Sachs and Mosebach, *Ber.*, 1911, 44, 2852).

## 78. Dyes derived from acenaphthenequinone and isatin : Fluoreno-acenaphthazines and fluoreno-indazines.

P. C. DUTTA, Muzaffarpur.

In continuation of the work of Dutta, Prasad and De on Fluoreno-phenanthrazines (*J. Indian Chem. Soc.*, 1932, 9, 211) the action of 1 : 2-diaminofluorene (Diels, Schill, and Tolson, *Ber.*, 1902, 35, 3284) on the aromatic o-diketones was further studied. The present communication deals with compounds produced by the condensations of diaminofluorene with acenaphthenequinone, isatin and their various derivatives. In the acenaphthenequinone series there is a distinct deepening of colour



as the nitro groups are introduced in the molecule and the shades produced on wool are deeper and much brighter than those of the Quinoxalino-acenaphthazines (Dutta and De, *Ber.*, 1931, 64, 2602), although the latter contained two azine rings. In the isatin series of course the compounds described presently, although some are highly coloured, impart lighter shade on wool than the corresponding Quinoxalino-indazines (Dutta and De, *loc. cit.*).

#### 79. Dyes derived from Quinoxalin dicarboxylic acid.

P. C. DUTTA, Muzaffarpur.

In studying the influence of nitrogen in the benzene ring on the colour and fluorescence of the phthalein dyes, it has been shown that the effect of such a nitrogen atom is to intensify the colour to a certain extent and to decrease appreciably the fluorescent property (Dutta and Tewari, *J. Indian Chem. Soc.*, 1926, 3, 161; 1927, 4, 201; De and Dutta, *Ber.*, 1931, 64, 2606).

To study further the above observations the present communication deals with phthalein dyes derived from Quinoxalin dicarboxylic acid (Hinsberg and König, *Ber.*, 1894, 27, 2185; *J.C.S.*, 1929, 645) by condensing with various aromatic amino and hydroxy compounds. Although the intensity of colour of these compounds was not studied quantitatively, the fluorescent property as expected has been found to be much diminished. As compared with the pyrazindicarboxyleins (De and Dutta, *loc. cit.*) the compounds described in this paper are lighter in colour presumably due to the less percentage of nitrogen.

#### 80. Condensation of aromatic o-hydroxyaldehydes with 3-hydroxythionaphthene.

P. C. DUTTA and S. C. DE, Muzaffarpur.

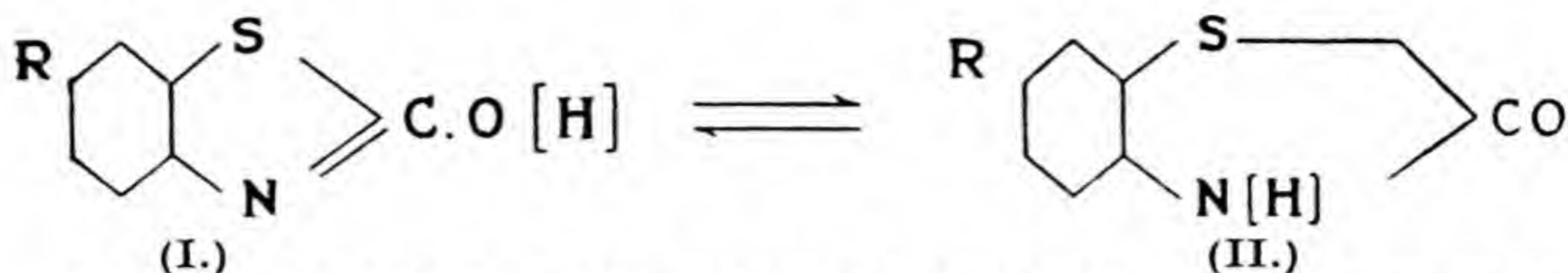
The present investigation deals with pyrylium compounds obtained by condensing 3-hydroxythionaphthene with aromatic o-hydroxyaldehydes, such as Salicylaldehyde, Resorcylic aldehyde, and 2-naphthol-1-aldehyde. Condensation was brought about in two ways (1) by passing dry gaseous hydrogen chloride through a methyl-alcoholic solution of the equimolecular quantities of the constituents when the substances separated out as crystals, and (2) by first preparing the o-hydroxy-styryl ketone—an intermediate product, and converting the latter into the pyrylium salts by the action of dry hydrogen chloride. In the case of 2-naphthol-1-aldehyde, the free pyrylium chloride which is brown coloured could not be isolated, as it soon decomposed in contact with air during filtration and so the corresponding ferri-chloride and the perchlorate which are quite stable were prepared.

#### 81. The unsaturation and tautomeric mobility of heterocyclic compounds. Part IV.—The mobility of the unsymmetrical triad system in 5-substituted-1-hydroxybenzthiazoles in relation to the ionotropic theory.

R. F. HUNTER and E. R. PARKEN, Aligarh.

Under conditions which are readily recognised as *ionising*, the 5-substituted-1-hydroxybenzthiazoles ( $I \rightleftharpoons II$ ) exhibit exclusive reactivity in the ketodihydro form (II) towards ordinary reagents. The same alkylation and acylation products are obtained from the mobile hydroxy derivatives as from their metallic derivatives in accordance with the theory discussed in Part III (Hunter and Jones, *J. Chem. Soc.*, 1930, 2190).



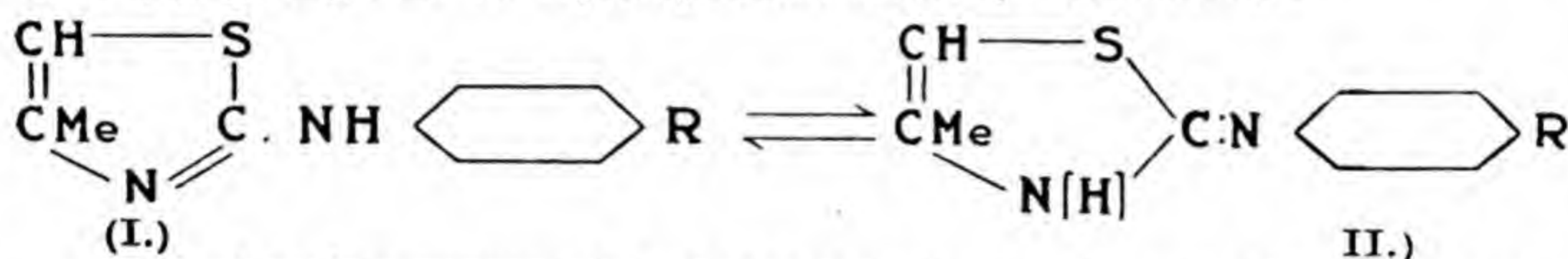


The ultra-violet absorption of mobile and static derivatives has also been examined on lines similar to those used in the case of the semi-cyclic amidines studied in Part III.

82. The unsaturation and tautomeric mobility of heterocyclic compounds. Part V.—The effect of aromatic conjugation on methylation of 2-*p*-substituted-anilinothiazole derivatives.

R. F. HUNTER and E. R. PARKEN, Aligarh.

The attraction of the aromatic nucleus on the  $\alpha\beta$ -double bond in the mobile 2-anilinothiazoles ( $\text{I} \rightleftharpoons \text{II}$ ;  $\text{R} = \text{OEt}$ ,  $\text{I}$ ,  $\text{Br}$ ,  $\text{Cl}$ ,  $\text{NO}_2$ ) is considerably less than in the 1-anilinobenzthiazoles (Hunter and Jones, *loc. cit.*) and these derivatives methylate exclusively in the amino aromatic form (I), giving rise to 2-phenylimino-3-methyl derivatives.

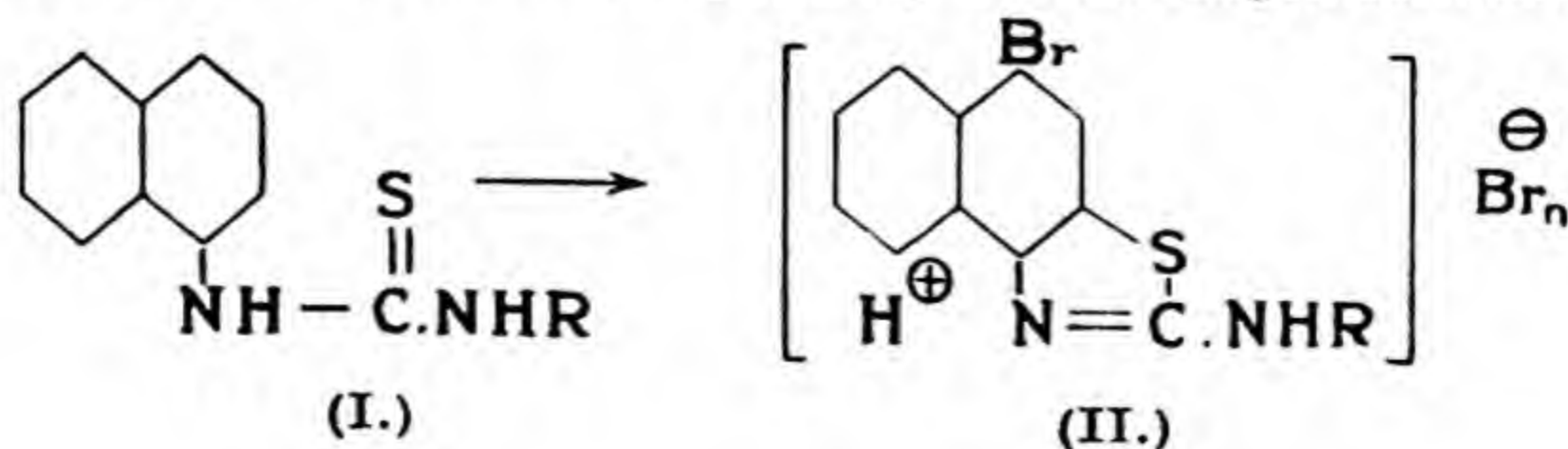


It is therefore suggested that a certain degree of aromatic character of the thiazole nucleus is lost when it is combined with a benzene ring as in benzthiazole. Since benzthiazole is a di-hetero derivative of naphthalene, this appears to constitute a further example of the mutual effect of aromatic nuclei, such as is seen in naphthalene itself, where neither of the presumably identical homocyclic carbon rings exhibits full benzenoid characteristics until the other is reduced as in the tetrahydro derivatives (Bamberger, *Annalen.*, 1890, 257, 1).

83. Studies in the Naphthathiazole series. Part I.—The constitution of the Bromo-addition compounds, of Bromo-substituted Alkylamino- $\beta$ -naphthathiazoles obtained in the bromination of *s*- $\alpha$ -Naphthylalkylthiocarbamides. The theory of the singlet linkage in relation to the apparent expansion of Valency groups.

CHIRAG HASAN and R. F. HUNTER, Aligarh.

It has been shown that the bromo-addition compounds of bromo-substituted-2-alkylamino- $\beta$ -naphthathiazoles obtained from the bromination of *s*- $\alpha$ -naphthylalkylthiocarbamides (I) are *hydropenta*-, *hydrotri*-, or *hydrodi-bromides* of the corresponding 8-bromonaphthathiazoles (II).





The hydropentabromides lose bromine yielding hydrotribromides, which in turn undergo degradation yielding the hydrodibromides which represent the most stable compounds of the series, despite the fact that their formulation necessitates the operation of a lone singlet linkage, such as

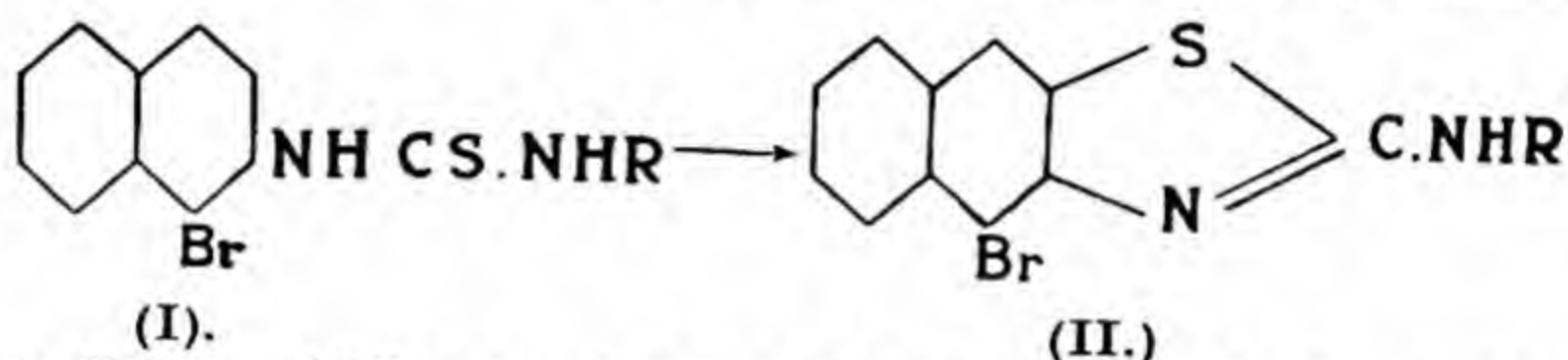
is present in the ion  $\text{H}_2^{\oplus}$ .

The formation of co-ordination compounds and the apparent expansion of valency groups such as occurs in compounds of the type of sulphur hexafluoride is discussed in the light of the theory of the single electronic link.

84. Studies in the Naphthathiazole series. Part II.—The synthesis of some derivatives of  $\beta\beta$ -Naphthathiazole.

CHIRAG HASAN and R. F. HUNTER, Aligarh.

The cyclisation of the bromo-substituted- $\beta$ -naphthylthiocarbamides (I) leading to the production of  $\beta\beta$ -naphthathiazoles (II) examined



under conditions similar to those yield in the synthesis of 8-bromo- $\beta$ -naphthathiazoles from the isomeric 4-bromo- $\alpha$ -naphthylthiocarbamides. The formation of the  $\beta\beta$ -naphthathiazole system is accomplished with considerably more difficulty than the isomeric  $\beta$ -naphthathiazole system, but this is probably partly conditioned by the inhibitory effect of the bromine *ortho* to the nitrogen atom which becomes nuclear in the process (compare Dyson, George, and Hunter, *J. Chem. Soc.*, 1926, 3041; 1927, 436).

85. The chemistry of the  $\psi$ -Thiohydantoins. Part I.—The bromination of Diphenyl- $\psi$ -thiohydantoin and its ortho-tolyl homologue.

M. OMAR FAROOQ and R. F. HUNTER, Aligarh.

It has been shown that the sulphur atom in the completely reduced thiazole nucleus in diphenyl- $\psi$ -thiohydantoin still retains the characteristic inertness of the sulphur atom in thiophen and benzthiazole, although in this case, there can be no question of the lone electrons being required for the completion of the sextuple group,  $6e$ , to which the aromatic character of such heterocyclic rings is ascribed (Armit and Robinson, *J. Chem. Soc.*, 1925, 127, 1605; Goss and Ingold, *J. Chem. Soc.*, 1928, 1268; Hunter, *J. Chem. Soc.*, 1930, 125).

86. Experiments on the synthesis of *Iso*-quinoline derivatives, Part II.

S. S. SILOOJA, K. S. NARANG, and J. N. RAY, Lahore.

It is possible that some of the minor opium alkaloids are homologues of papaverine and laudanosine. Homo-laudanosines have been synthesised by the routine method and the colour reaction of some of the synthetic bases are very similar to meconidine. Direct comparison would be instituted as soon as some natural base is available. 1-methyl 3:4-dihydro-6:7-methylenedioxy-isoquinoline condenses with nitro-aldehydes to give the styryl derivatives but an ordinary aldehyde does not.



## 87. The constitution of Vasicine. Part II.

T. P. GHOSH, S. KRISHNA, K. S. NARANG, and J. N. RAY, Lahore.

Further experiments on the oxidation of natural vasicine have furnished clue as to its constitution. It is 2-allyl-4-oxy-1 : 2-dihydro-quinalzoline. Vasicine isomerises to a cyclic body in presence of alkali to give *iso*-vasicine. The same change takes place initially in the formation of vasicine-methiodide which is identical with the methiodide formed directly from *iso*-vasicine. *Iso*-vasicine gives an amino oxide with hydrogen peroxide. The structures of different oxidation products are discussed.

## 88. Experiments on the synthesis of Cyanomaclurin.

A. L. BHALLA and J. N. RAY, Lahore.

O-methoxy-2 : 4-dihydroxy-phenpriopiophenone does not smoothly pass to a flavane.

Salicylidine-acetophenone, salicylidine-2 : 4-dioxyacetophenone, 2-hydroxy-4 : 6-dimethoxy-benzilidene-2' : 4'-dimethoxy-acetophenone, are catalytically reduced to the corresponding dihydro bodies. These seem to be flavanes with a molecule of water co-ordinated at the basic oxygen atom and like cyanomaclurin are converted to amorphous bodies on treatment with hot dilute mineral acids. Therefore this route is not suitable for the synthesis of cyanomaclurin. 3 : 5 : 7 : 2' : 4'-penta-methoxy-benzopyrillium chloride (from  $\omega$ -methoxy-resacetophenone-dimethyl-ether and phloroglucinaldehyde-dimethyl ether) is converted by catalytic reduction to 3 : 5 : 7 : 2' : 4'-pentamethoxy-2 : 3-dihydro flavane (dihydro-cyanomaclurin-penta-methyl ether). Identity would be established by direct comparison when some cyanomaclurin is available.

## 89. Studies in Chemotherapy. Part IV.

B. D. KOCHHAR and J. N. RAY, Lahore.

1-aceto-2-naphthol has been condensed with o-nitro-aromatic aldehydes. The products on reduction pass to 2'-hydroxy-naphthyl-quinolines. These are being tested for antimalarial properties because Fourneau has recently shown that a simple naphthalene derivative has antimalarial properties.

## 90. Studies in Chemotherapy. Part V.

K. N. KAUL and J. N. RAY, Lahore.

Further derivatives of cotarnine containing a quinoline nucleus have been synthesised for the purpose stated in the title.

91. Experiments on the synthesis of *Iso*-bergapten.

J. N. RAY, Lahore.

6-hydroxy-benzfurfurane has been converted into the corresponding o-hydroxy aldehyde. This condenses with malonic acid (in pyridin and piperidine) to give the corresponding coumarin. The product has the ring systems of *iso*-bergapten.

## 92. Further experiments on the synthesis of Brazilin.

J. N. RAY, Lahore.



93. The influence of attached rings on the formation and stability of heterocyclic compounds. Part III.

T. N. GHOSH, Bangalore.

In continuation of last year's work (*Proceedings Indian Science Congress, 1932, Section of Chemistry*), some aryl-carbamidopropionic acids have been prepared which, on treatment with acetic anhydride, yield oxazine derivatives. Similarly some new benzoxazine derivatives have been prepared. The evidence obtained from the action of hydrolysing agents on the above oxazine derivatives and  $\beta$ -lactylurea on the one hand, and benzoxazine derivatives on the other, points to the well-marked influence of the benzene ring in increasing the stability of the heterocyclic system. The remarkable stability of an eight-membered lactone ring obtained from salicylidene-anthranilic acid is attributed to the presence of two benzene rings. This behaviour of the benzene ring in helping ring-formation can be explained by the recent theory of Mills and Nixon (*J.C.S.*, 1930, 2510) which states that, round the benzene ring, adjacent valencies will be nearer where the corresponding carbon atoms are joined by a single bond.

94. Studies in heterocyclic compounds.

T. N. GHOSH, Bangalore.

By reacting o-phenylenediamine, naphthylenediamine with semi-carbazides, some triazine derivatives have been obtained, the constitution of which has been discussed. The reaction of carbohydrazide upon o-phenylenediamine, yields an aminotriazine derivative which further reacts with carbimides to give rise to complex ring-systems. A hepta-triazine derivative has been obtained by reacting anthranilic acid with semi-carbazide.

95. Studies in heterocyclic compounds.

A. C. SIRCAR and I. B. PAL, Calcutta.

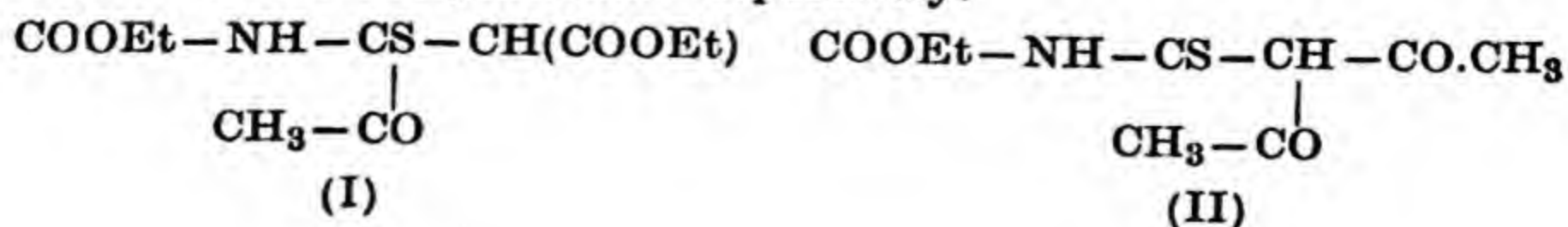
The paper describes the preparation of a number of different types of diheterocyclic compounds from  $\alpha$ - $\beta$ -diamino-quinoxaline, which already contains an azine ring the object being to study how in compounds containing two dissimilar adjacent heterocyclic rings in their molecules the properties of the different heterocyclic nuclei are affected by one another and how the properties of such compounds differ from those of the corresponding compounds in which the two heterocyclic nuclei are separated by a benzene ring.

96. New methods of synthesis of Pyridine derivatives.

T. N. GHOSH and P. C. GUHA, Bangalore.

(1)  $\delta$ -Chloro- $\beta$ -ketobutane has been prepared from  $\beta$ -chloro-propionylchloride and zinc-methyliodide (Blaise and Maire *Bl.* [4], 3, 270) and its condensation with Na-urethane is being tried with the expectation that the resulting product will yield a pyridine derivative on treatment with Na-ethylate.

(2) Compounds of the types (I and II) have been synthesised by the action of carbethoxythiocarbimide on the sodium derivatives of acetoacetic ester and acetylacetone respectively.





With a view to synthesise pyridine compounds by the elimination of a molecule of alcohol, the action of Na-ethylate is being tried upon them.

97. Synthesis of Quinoline derivatives. Part I.—Extension of Beyer's synthesis of Quinoline derivatives.

D. N. MAZUMDAR, Bangalore.

Quinoline synthesis, according to Beyer's reaction, has not been studied with aromatic aldehydes and substituted amines. So a study of the same with benzaldehyde, piperonal and anisaldehyde has been made and in each case a product has been obtained though in poor yield. All these compounds respond to the ordinary tests for alkaloids.

The product obtained in the case of anisaldehyde gives a picrate m.p. 140°C. with shrinkage at 137°C.

98. Semi-micro determination of carbon and hydrogen, and nitrogen in organic substances.

B. L. MANJUNATH and S. SIDDAPPA, Bangalore.

The paper deals with the simplification of the apparatus and methods of Bobranski and Sucharda (*Sammlung Vieweg*, Heft 94, 1929). Quantities of material required are from 0.02 to 0.03g. and the average time required for analysis is about one hour and a quarter. Very accurate results have been obtained even by beginners. The paper has been communicated with the object of drawing attention to a more general adoption of semi-micro methods in regular laboratory training. Further, the introduction of such a course will serve as a valuable preliminary to micro-analytical work.

99. Quinaldinic acid as an analytical reagent. Part II.

P. R. RAY and M. K. BOSE, Calcutta.

In extension of our previous work, quinaldinic acid has been employed with excellent results for the separation of copper from phosphoric acid, manganese, nickel, cobalt, lead, arsenious and arsenic acids. Equally good results have also been obtained in the separation of zinc from manganese, calcium, barium, magnesium and phosphoric acid. The use of the reagent for the micro-detection and colorimetric estimation of iron has been described.

100. Estimation of tannin in *Cassia Auriculata*.

N. SRINIVASAN, Bangalore.

The method involves the use of the Pulfrich Refractometer for measurements of the differences between the angular positions for the extracts and their nontans. The conditions for obtaining clear extracts, and the detannisation by pure casein, have been standardised and adapted for small scale work. Within limits, the tan strengths of different solutions as obtained by evaporations are related in a simple way to the corresponding angular differences. This relationship which is being tested in low concentrations is expected to provide a rapid analytical procedure in physiological studies concerning the formation and accumulation of tannin in the bark of this plant.

101. Hydroxy-anthraquinones related to Aloe-emodin. Part I.

P. C. MITTER and SUMATICHAND BACHHWAT, Calcutta.

The acetyl derivative of 1-hydroxy-3-methyl-anthraquinone can be converted into the corresponding carboxylic acid by oxidation with



chromic acid. On treatment with thionyl chloride, the acid is converted into the chloride which on reduction with hydrogen in presence of palladiumised barium sulphate, gives the corresponding aldehyde. On deacetylation and reduction with hydrogen in presence of platinum oxide, the aldehyde is converted into 1-hydroxy-anthraquinone 3-carbinol.

102. Hydroxy-anthraquinones related to Aloe-emodin. Part II.  
P. C. MITTER and S. J. DAS-GUPTA, Calcutta.

The acetyl derivative of 1-hydroxy-6-methyl anthraquinone can be converted into 1-hydroxy-anthraquinone-6-carboxylic acid, 1-hydroxy-anthraquinone-6-aldehyde and 1-hydroxy-anthraquinone-6-carbinol in the same manner as in the foregoing.

103. The Budde effect in halogens. Part I.—Chlorine.  
TATA SURYANARAYANA, Bangalore.

Experiments on the action of light in pure moist and dry chlorine have been conducted, pressure changes being recorded by a highly sensitive all-glass-spring-manometer.

The following results have been obtained :—

(1) The Budde effect which is present in moist chlorine rapidly diminishes on drying the gas.

(2) The effect is most marked towards the ultra-violet and disappears altogether for light of wavelength greater than 5,000 A.U.

(3) Increase in pressure, on illumination, has been observed at different pressures, the change being approximately proportional to the pressure.

104. Period of induction in chemical reactions. Part IV.—  
Action of phosphorous acid on alkali bromate and iodate.

P. NEOGI, BENOYENDRA NATH SEN, and SUDHAMOY  
MUKHERJI, Calcutta.

Further work on the period of induction observed in the action of phosphorous acid on alkali bromate and iodate has been done and the results obtained are in agreement with those recorded in previous papers (Neogi and Neogi, *J.C.S.*, 1927, 131, 30 and subsequent papers) relating to the period of induction observed in the ionic reactions already studied.

105. The dissociation pressure of cadmium carbonate.  
P. Y. NARAYANA, Bangalore.

The dissociation of pure cadmium carbonate has been studied by the static method in the temperature range 260–360°C. The pressure of carbon dioxide obtained can be fairly accurately represented by the equation

$$\log p = 0.014T - 5.916.$$

These values differ considerably from those of previous observers. The heat of reaction calculated by means of Nernst's equation approximates to the thermochemical value.

At lower temperatures the rate of establishment of equilibrium is very slow and the pressure appears to depend on the amount of oxide in the solid phase.



## 106. Theory of Liesegang phenomena by evaporation from walls.

H. P. CHOWDHURY and SATYENDRA RAY, Lucknow.

Liesegang deposits have been observed by the authors by dipping strips or blocks of tied blotting papers in red ink or inorganic salt solutions.

These phenomena under the conditions can be explained by applying an analogue of the well-known formula of heat conduction :—

$$dq = -KA \left( \frac{dc}{dx} \right) dt.$$

where C = the concentration going across a section.

A periodic variation of C, the concentration, with height can be obtained by assuming the loss of water from the face exposed to the atmosphere to be proportional to the vapour pressure and therefore to the factor  $(1 - RC)$ .

Closer or more distant rings or layers found in the Liesegang phenomena can be explained on the basis of the results thus obtained. The effect of wetting the block as well as of the humidity of the atmosphere as indicated by the theory has also been qualitatively verified.

## 107. The system sodium sulphite—sodium thiosulphate—water.

S. G. KIRI and K. R. KRISHNASWAMI, Bangalore.

The solubility of sodium thiosulphate in sodium sulphite solutions of various concentrations has been determined in the temperature range 21–45°, and the results obtained are discussed in the paper.

## 108. The activation of Indian charcoals.

L. GOPALA RAO, Bangalore.

Specimens of charcoal from eleven kinds of wood have been activated under different conditions and tested as regards their power of decolourising sugar solutions. It has been found that although the removal of mineral constituents by means of acid is an advantage, satisfactory charcoals can be obtained without the employment of this costly process. Except in one or two cases the species of wood does not have much influence on the quality of the charcoal.

A furnace for continuous activation has been constructed affording data for the design of activating plant of commercial type.

## 109. Adsorption of electrolytes by activated charcoal.

J. N. MUKHERJEE, S. P. ROYCHOU DHURY, and MONOMO HON MAJUMDAR, Calcutta.

Experiments have been carried out with activated ash-free sugar charcoal. It has been shown that on washing, the charge of sugar charcoal changes from negative to zero before the charcoal ultimately acquires a positive charge. The change of charge on the surface of charcoal has been shown to be due to electrolytic impurities coming out of the charcoal surface. Adsorption of acid and alkali by the charcoal has been determined by indicator titrations and also by conductivity measurements and conductometric titrations of the supernatant liquid remaining after adsorption. The slope of the conductometric titration curves of the clear supernatant liquid shows that weak anions or cations are not present in the supernatant liquid after adsorption. It is found that on washing, the adsorption of alkali by charcoal definitely diminishes, but



that of hydrochloric acid remains unchanged. Also both negative and neutral charcoals have been found to adsorb hydrochloric acid very strongly. Sulphuric acid is, however, very slightly adsorbed. Both hydrochloric and sulphuric acids give almost the same electro-osmotic effect on negative charcoal.

# 110. Studies in some physico-chemical properties of gels, Part III.

N. A. YAJNIK, D. N. GOYLE, and J. D. VARMA, Lahore.

A study of the physico-chemical properties of some more gels—both of organic as well as of inorganic substances—has been continued with a view to arrive at their structure. Amongst the properties already studied by the authors, two more—(i) the relation between the time of setting and surface tension, and (ii) the double refraction of light by gels—have been included in the present investigation. Further investigations on the diffraction of X-rays by different gels is being continued.

# 111. Sensitivity of sols and its relation to the particle-size.

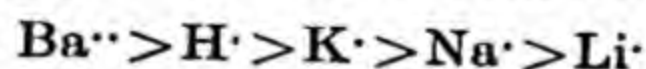
N. A. YAJNIK, D. N. GOYLE, and G. C. DANG, Lahore.

The coagulation of sols—filtered through filter papers of known porosity—by electrolytes has been studied and it has been found that the filtered sols show a more regular coagulation than the unfiltered ones. Further, the stability of the sols goes on increasing as they are filtered through finer media, other factors remaining the same.

# 112. Variation of the charge of colloidal particles. V—Experiments on arsenious sulphide sol in relation to the critical potential.

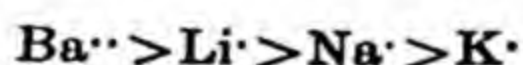
J. N. MUKHERJEE, S. P. ROYCHOU DHURY, and S. G. RAJKUMAR, Calcutta.

Cataphoretic measurements on arsenious sulphide sol have been carried out by the following electrolytes:  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{HCl}$ ,  $\text{BaCl}_2$  and  $\text{As}_2\text{O}_3$ . From the speed-concentration curves it is found that the adsorbability of the various cations by the sol is in the following order for the ascending portions of the curves:



The adsorption of  $\text{Ba}^{++}$  and  $\text{H}^+$  ions are so strong that under no condition, that of chlorine can outweigh them and a continuous decrease in charge is observed (negative slope).

In the portions of the curves where the concentration is lower than  $\cdot 01$  normal, the adsorbability of the different cations appears to be in the following order:



The curve for  $\text{HCl}$  cuts the other curves and indicates that the relative adsorbability of  $\text{H}^+$  ion changes with concentration even within this region.

With  $\text{As}_2\text{O}_3$  an initial increase in cataphoretic speed at  $\cdot 0001$  N and at higher concentration a continuous decrease is observed.



113. Colloid chemical analysis of various samples of aluminium hydroxide sols.

S. P. ROYCHOUDHURY, Calcutta.

Colloid chemical analyses of various aluminium hydroxide sols of very low specific conductivity have been carried out. The results show that the observed specific conductivity of the sol is much less than the calculated sum of the contributions to the specific conductivity by the various ionic species ( $H^+$ ,  $Cl^-$ ,  $1/3 Al^{+++}$ ) present in the sol.

114. Replacement of adsorbed ions on the surface of activated silica gel.

P. B. GANGULY, Patna.

A specimen of silica gel was activated by the method used by Ray (*Jour. Phys. Chem.*, 1925, 29, 79). The adsorption of the positive ions from electrolyte solutions by the activated silica gel was measured in the cases of about twenty different electrolytes. In the case of monovalent electrolytes an ion of a metal of lower atomic weight can generally be replaced by that of a metal of heavier atomic weight. The extent of replacement depends on the concentration of the solution, valency of the ions and the relative weights of the adsorbed and displaced ions. The amount of adsorption as also the subsequent replacement by a heavier ion depends on the mode of formation and activation of the gel. The results have been discussed in the light of ionic replacements in soils.

115. Determination of flocculation values from measurements of the rate of coagulation of an arsenious sulphide sol.

D. N. GHOSH and P. B. GANGULY, Patna.

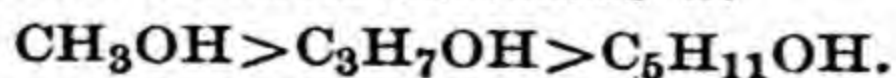
Numerous investigators have determined flocculation values from measurements of the time required for the production of a certain state of turbidity of the sol. Flocculation values thus determined are not strictly comparable as they refer to a transitory state, during the process of coagulation. It is much more important to measure the velocity of coagulation as coagulation is really a process of the progressive growth of particles. An experimental arrangement has been set up for determining the rate of coagulation of colloidal solutions by measuring the change in the intensity of the scattered beam. Flocculation values determined by the above method agreed well with the experimental measurements of Oden and Weiser.

116. Studies in ceric hydroxide sol.

MATA PRASAD and M. V. NABAR, Bombay.

The kinetics of coagulation of the ceric hydroxide sol dialysed and diluted to different extent has been studied when the sol is coagulated by different amounts of sodium and magnesium chlorides. The coagulation velocity curves are 'S' shaped for impure and the concentrated sols, and steep for the pure and the diluted ones. Smoluchowski's equation is applicable up to a certain stage of coalescence of the ceric hydroxide particles. Larger deviations are observed with pure sol and with sol coagulated with large amount of the electrolytes.

The alcohols sensitise and the sugars protect the coagulation of the sol by sodium chloride: these actions increase as the sol gets purer. The sensitising action of alcohols increases as



Cane sugar acts as a better protecting agent than any other sugar.



## 117. The kinetics of coagulation of titanium dioxide sol.

S. M. MEHTA and MISS OLIVE JOSEPH, Bombay.

The coagulation of titanium dioxide sol by sodium and magnesium chlorides has been studied when the sol is dialysed and diluted to different extent. The Smoluchowski's equation has been found to apply to the coagulation of titanium dioxide sol only for a limited range of the concentration of the coagulator. The coagulation velocity curves are 'S' shaped for sols dialysed up to ten days; sols dialysed for longer time do not show the auto-catalytic nature of the coagulation process. These results have been explained on Freundlich's first and second critical potential.

## 118. Variation of viscosity during coagulation. Part I.

S. S. JOSHI and K. S. VISHVANATH, Benares.

Progress of the coagulations of colloid arsenious sulphide by a number of KCl solutions in the range, N/16 to N/20 when the above sol was protected by 0.025% and 0.05% gelatine solutions, by BaCl<sub>2</sub>, whose concentration was varied progressively from N/11.7 to N/10, and of 0.1% and 0.05% gelatine solutions by KCl in the range N to N/2 was studied by following the viscosity variation. It was observed that in all cases viscosity diminished to a minimum. This initial fall increases by increasing the coagulator concentration. The interval of time within which, during coagulation, the viscosity of the system lies below the initial value (that is, at the start of coagulation) increases rapidly as the coagulator concentration is reduced. Evidence has also been obtained of the existence of more than one minimum in the viscosity-time curve when very low concentrations of the coagulator were employed.

## 119. Variation of viscosity during coagulation. Part II.

S. S. JOSHI and T. MADHAVA MENON, Benares.

In order to obtain more information about the conditions of the viscosity diminution in the coagulating sol (*cf.* Part I), work was extended to coagulations in which various concentrations of each of the following electrolytes were used: KF, KCl, KBr, KI, BaCl<sub>2</sub>, AlCl<sub>3</sub> and ThCl<sub>4</sub>. For a given concentration of any of the foregoing coagulators, coagulations were studied over a wide range of the colloid concentration. It was found that the deduction made in Part I, met with an occasional exception when ThCl<sub>4</sub>, AlCl<sub>3</sub> and KF were used. The magnitude of the initial fall did not show any regularity of variation in the KF, KCl, KBr and KI series. The same remark applies to the influence of varying the colloid concentration, keeping that of the coagulator constant. It can be stated in general that the viscosity-time curves show less inflexions as the concentration of the coagulator is increased. For low concentrations, evidence obtained is very appreciable to show that the corresponding process of coagulations passes through a series of successive zones of coagulation, each with a characteristic time rate for its viscosity variation.

## 120. Studies in the kinetics of coagulation. Part V.—The 'Wall Effect'.

S. S. JOSHI and V. LAXMI NARAYAN, Benares.

Evidence showing that the walls of the containing vessel cannot be considered as but an inert component of a colloid system was afforded (Joshi and T. Surya Narayan, *J. Indian Chem. Soc.*, 1930, 7, 883; also *Koll. Zeit.*, 1932, LIX, 335) by the observation that the characteristic



precipitation of the colloid manganese dioxide on the parchment paper during dialysis was very markedly reduced by applying a negative potential of about 200 volts to the dialysing septum. This possibility of 'wall effect' has now been examined in detail in the coagulations of manganese dioxide, antimony sulphide and ferric hydroxide sols, under a wide range of conditions. The 'wall effect' was observed by following the course of any given coagulation (a) with the normal wall area of containing vessel, and (b) when this was increased about fourfold by introducing smooth glass beads of known size, and (c) when the containing walls and beads were paraffined. A number of these coagulations were found to be autocatalytic, as judged from the rise in  $\beta$  with time, and the corresponding coagulation-time curve being s-shaped. The coagulation rate increased markedly and autocatalysis diminished under (b). Just the opposite was observed under (c). In general the course of coagulation becomes simplified under (b), and is assignable as belonging to the region of 'rapid' or the 'slow' coagulation as contemplated in Smoluchowsky's theory. It is considered that 'autocatalysis' is not fundamental to the process of coagulation, in general. In view of the well-known limitations of the applicability of Smoluchowsky's theory in the region of *slow* coagulation, numerous workers have suggested 'autocatalysis' as the main characteristic of slow coagulations in contradistinction to the mechanism underlying Smoluchowsky's analysis. Results obtained in this investigation show that autocatalysis can be eliminated and added on to the course of a given coagulation by manipulating factors (such as 'wall effect') not fundamental (on the existing theories at any rate of the kinetics of coagulation), to the main process. The disentanglement of a coagulation from such a factor must therefore precede its examination in respect of the applicability of Smoluchowsky's theory. It was found for example in the coagulation of ferric hydroxide sol by potassium chloride solutions that within about 50 minutes from the start of coagulation  $\beta$  increased by about ten times, the coagulation-time curve being markedly s-shaped, indicative of autocatalysis. That the last-named factor had masked the true course of the reaction was shown by the fact that when the same coagulation was studied with increased wall surface, the s-shape had disappeared, and concordant values for the Smoluchowsky's constant,  $\beta$ , were obtained.

## 121. Studies in the coagulation of colloids from the standpoint of Smoluchowski's theory. Part VI.

S. S. JOSHI and A. N. LAL, Benares.

It was observed in Part II (*J. Indian Chem. Soc.*, 1931, 8, 337) and Part III (*Ibid.*, 1932, 9, 157) of this series that in the *slow* coagulations of the arsenious sulphide sol by dilute sulphuric acid solutions, the departure from the requirements of Smoluchowsky's theory (as shown by the diminution in  $\beta$ ) occurred in all the cases examined during the *initial* stages of coagulation. The following equation was used:

$$\beta = \frac{1}{t} \left[ \left( \frac{n_0}{n_t} \right)^{\frac{1}{2}} - 1 \right] \quad \dots \dots \dots (i)$$

where the different symbols have their usual significance. This result is contradictory to the findings of Mukherji and Majumdar (*J. Chem. Soc.*, 1924, 125, 785), Desai (*Trans. Faraday Soc.*, 1928, 24, 191) and others who used the equation

$$\Sigma n = n_0 / 1 + \beta t \quad \dots \dots \dots (ii).$$

A study was made, therefore, of the coagulations of colloid manganese dioxide, using a different method of following the course of coagulation, viz. the change of the surface tension of the coagulating sol. It was found



that using equation (i) same results were obtained as were observed previously (*loc. cit.*). Applying equation (ii) to the same data, it was found that in agreement with the results of workers mentioned above, just the opposite was found to be the case. This apparant anamoly has been discussed in the paper from a theoretical point of view.

## 122. The preparation of manganese dioxide sol.

M. K. SHRINAVASAN, Benares.

In view of its well-known and characteristic instability, work was undertaken to investigate the possibility of preparing concentrated and stable sols of manganese dioxide, using glycerol, gelatine, sodium oleate, egg white and casein as protectives. For reasons explained in the paper trials with a number of concentrations of glycerol, gelatine and sodium oleate gave sols of but poor concentration. This is rather unexpected in view of the well-known strength of gelatine and sodium oleate as protectors. Best results were obtained with gum arabic and egg white (under restricted conditions of preparation detailed in the paper). The resulting sols were concentrated and what is more, could be filtered and dialysed without coagulation.

## 123. Studies in the protective action of colloids. Part I.— Ionic adsorption in coagulations of protected sols.

A. JOGA RAO, Benares.

A review of the literature having shown that no quantitative information was available on the subject, the present work was undertaken with a view to correlate (i) the amount of ionic adsorption with the concentration of the protective agent in the system. Arsenious sulphide sols protected by different concentrations of gelatine, sodium oleate, and starch solutions were coagulated by barium and ferric chloride solutions, the concentration of the coagulator being also varied. The amount of ionic adsorption produced was then determined analytically. Results showed in a number of cases that the adsorption on the colloid actually diminished despite an increase in the concentration of the protector. The corresponding curves also show a number of breaks which have been ascribed to the formation of adsorption complexes.

## 124. Studies in the protective action of colloids. Part II.— Variation of some physical properties of protected arsenious sulphide sol with the concentration of the protector.

A. JOGA RAO, Benares.

The work in Part I has been extended to a study of the (i) viscosity, (ii) turbidity, (iii) surface tension, and (iv) refractive index measurements for different values of the protector concentration. Owing to experimental difficulties results with the last two properties have not been decisive. Viscosity measurements have in the main confirmed the conclusions in Part I.

## 125. A new method of investigating the kinetics of alcoholysis.

S. S. JOSHI and A. JOGA RAO, Benares.

Despite the considerable amount of work which has been carried out by numerous workers on the above subject, but little quantitative information is available on the kinetics of this reaction with a few notable exceptions. The kinetics of the alcoholysis of methyl acetate by amyl,



isobutyl, and n-propyl alcohol were studied by following the viscosity variation of the mixture at two temperatures with the Scarpa type of viscometer, and also using different amounts of hydrogen chloride as a catalyst. In agreement with Kolhatker's results (*J.C.S.*, 1915, 107, 921) the reactions were found to be unimolecular, and the velocity constant proportional to the concentration of the catalyst. Interesting results were obtained when isobutyl alcohol was used at 25°C. Plotting log of concentration against time, two straight lines inclined at an angle were obtained, giving two series of values for the velocity constant. This feature disappeared when the same reaction was carried out at 30°C. Results similar to the previous case were obtained at 30°C. in the alcoholysis by normal propyl alcohol. A *tentative* suggestion has been made that those reactions proceed in two consecutive stages.

126. Distribution of benzoic acid between toluene and water in the presence of electrolytes.

S. S. JOSHI and K. P. HALDAR, Benares.

The distribution of benzoic acid between toluene and water was studied when the latter contained varying amounts of NaCl, KCl, BaCl<sub>2</sub>, CaCl<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>4</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>, Th(NO<sub>3</sub>)<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl. It was found that *k*, the distribution coefficient fell progressively as the amount of the electrolyte added was increased in the case of the first four salts and sulphuric acid. This diminution was exactly linear in the case of KCl. *k* remained constant with varying amounts of Ce(NO<sub>3</sub>)<sub>4</sub> and Th(NO<sub>3</sub>)<sub>4</sub> present in the aqueous phase. In the case of HCl and HNO<sub>3</sub>, *k* diminished to a minimum which remained unaltered with further and large additions of the acid to the water, the value of the constant minimum being the same in both the series. Interesting results were obtained when *k* was determined with a given amount of KCl in the aqueous phase: this amount was varied for different series. It was found that with KCl, *k* increased to a *maximum* and then diminished. Just the *reverse* was the case with BaCl<sub>2</sub>, which gave *minima*. It must be pointed out here that within the range of benzoic acid concentrations used, when the aqueous phase was pure water, *k* was constant. Experiments were also carried out to investigate the influence on the solubility of benzoic acid in water in the presence of the salts mentioned above. An attempt has been made to relate the above results with the ionic strength, the state of hydration of the added electrolytes, the variable ionisation of benzoic acid in the aqueous layer and its polymerisation in the toluene layer.

127. Kinetics of sucrose inversion, produced adiabatically.

S. S. JOSHI and GURUDAS R. PHANSALKER, Benares.

Arising out of some work on the energetics of sucrose inversion, it was observed that when the reaction occurred adiabatically, the heat capacity of the system being sensibly constant, fairly concordant values for the unimolecular coefficient were obtained for variously concentrated sucrose solutions, from a knowledge of the gradients of the time-temperature curves. The temperature interval was about one degree C., and the accuracy of the measurement was about 1 in 3,000. It is considered that the method is particularly useful in investigating the initial stages of a reaction.

128. Decomposition of paraffins in electric discharge.

S. S. JOSHI and SARJU PRASAD, Benares.

Thin layers of molten paraffins were subjected to ionisation by collision in fields due to continuous, and alternating (at commercial



frequencies) potentials. Under the available conditions of electric supply, the decomposition of the paraffins was more appreciable under the former conditions. The final mixture consisted principally of hydrogen, methane, acetylene, and ethylene. Data are given, when the reaction was carried out in (i) vacuum, (ii) in nitrogen, and (iii) hydrogen. The electrical conditions were varied in respect of the (i) applied voltage, (ii) the secondary current, (iii) the frequency, and (iv) the capacity introduced in the high tension circuit. All these factors were found to influence both the rate of change and the composition of the reaction mixture. The progress of the decomposition was followed by (i) the pressure-time curves, and (ii) by analyses of the mixtures at different stages of the decomposition.

129. Kinetics of the decomposition of trichloroacetic acid in aniline.

A. N. KAPPANNA and H. W. PATWARDHAN, Nagpur.

A study of the kinetics of the decomposition of trichloroacetic acid in aniline and aniline-benzene and aniline-toluene mixtures has been made. Benzene and toluene are inert so far as trichloroacetic acid decomposition is concerned. For the same concentration of the acid, the velocity of decomposition of the acid diminishes with diminution of aniline concentration in the mixtures. The results obtained, indicate that aniline molecules take part in activating the trichloroacetic acid molecule and the order of reaction, with respect to aniline, has been found to be two.

130. The photo-reduction of ferric chloride in alcoholic solutions.

MATA PRASAD and P. S. LIMAYE, Bombay.

The photo-reduction of alcoholic solutions of ferric chloride in (a) sunlight, and (b) artificial light takes place in two stages. The order of the photo-reduction in the first stage, in both the cases, is zero molecular but in the second stage, it is unimolecular in the first case and zero molecular in the second. The extinction coefficient measurements of the solutions exposed to artificial light and the conductivity measurements of solutions exposed to sunlight also show a sudden decrease in value after some time. The change in the stage of the reduction from one to the other is not due to the formation of colloidal ferric hydroxide, as it has been found to retard the reduction in both the stages. In sunlight, lower wavelengths are more active and greater reduction takes place in composite light than that in its separate constituents.

The value of the quantum efficiency for solutions of concentrations between 0.1 M. and 0.2 M. lies between 1 and 3 at 30° for radiations lying in the visible region and it increases with (i) temperature, (ii) concentration of the solution, and (iii) frequency of the incident light.

131. Note on electrical adsorption.

A. GANGULI, Chandernagore.

In a previous paper [Kar and Ganguli, *Zeit. fur. Phy.*, 61, 411 (1930); Ganguli, *Ind. Phy. Math.*, 3, 53 (1923)] Langmuir's equation was extended to derive expressions for electrical adsorption. There we assumed the simultaneous adsorption of the similarly charged ions as well. The ionic antagonism, initial increase of charge of colloidal particles, charge reversal, anomaly of the valency rule can only be explained on the assumption that besides electrostatic forces, the physico-chemical adsorption



forces are also in operation [cf. Dhar, *J.I.C.S.*, 4, 173 (1927)]. In the case of anomalous behaviour of colloidal solutions and dilution again, the adsorption of like ions must be taken into account.

Previously, we simplified the equations by neglecting the area correction. Proceeding in the rigorous manner we obtained the charge due to adsorption of uni-univalent ion

$$\eta = \frac{F}{\beta + \beta^1} \left\{ \frac{1}{1 + \frac{k_1}{c} e^{-\frac{Q_1 + F\psi}{RT}}} - \frac{1}{1 + \frac{k_2}{c} e^{-\frac{Q_2 - F\psi}{RT}}} \right\}$$

where  $k_1 = \frac{(2\pi m_1 RT)^{\frac{1}{2}}}{Nh(\beta + \beta^1)}$  and  $k_2 = \frac{(2\pi m_2 RT)^{\frac{1}{2}}}{Nh(\beta + \beta^1)}$ .

On assuming for  $\eta=0$ ,  $\psi=0$ , we obtain the simple equation deduced before.

In order to have net electric charge we are to introduce another factor  $\eta_2$  corresponding to Debye-Huckely expression for interionic attraction [cf. Muller, *Koll. Chem. Bei* 26, 274 (1928)]

$$\eta_2 = \frac{\sqrt{DRTc}}{2\pi} \left( e^{\frac{F\psi}{2RT}} - e^{-\frac{F\psi}{2RT}} \right)$$

or  $\eta_0 = \eta_1 + \eta_2 = \frac{2F^2c\psi}{kRT} + \frac{\sqrt{DRTc}}{2\pi} \frac{F\psi}{RT}$ .

From Debye's theory  $\psi = -\alpha \sqrt{c}$

the electro-kinetic potential decreases as  $\sqrt{c}$ . The evaluation of  $\psi$  also involves the dielectric constant and there are controversies as to whether the dielectric constant of the bulk of the medium or that of the liquid enclosed within the double layer is to be chosen. Neglecting the effect of similarly charged ions, the effect of the valency ( $z_i$ ) coagulating ions will be indicated by the exponential factor  $e^{-z_i}$ . Thus the coagulating concentrations of mono-, bi-, tri-, and tetravalent ions will be as

$$c_1 : c_2 : c_3 : c_4 = e^{-\frac{F\psi}{RT}} : e^{-\frac{2F\psi}{RT}} : e^{-\frac{3F\psi}{RT}} : e^{-\frac{4F\psi}{RT}}.$$

## 132. Note on adsorption of gases by solids.

A. GANGULI, Chandernagore.

In previous papers Langmuir's adsorption formulæ were derived by the author for the two cases, when an adsorbate molecule occupied (1) only one-adsorption centre, (2)  $n$ -adsorption centres. For the second case, surface dissociation of adsorbate molecules was proposed. It was shown that the maximum adsorption potential of Polanyi corresponded to the heat of adsorption. Recently London [*Z. Phys. Chem.*, 11B, 222 (1930)] has given a wave-mechanical method for calculating heat of adsorption, and it has been shown that the agreement between observed and theoretical values are obtained for mono-molecular layer. This confirms our assumption that although there is a theoretical possibility of change of adsorption potential with the distance, the value for the distance corresponding to unimolecular adsorption is of importance, i.e. the maximum adsorption potential is identical with the heat of



adsorption. The fundamental difference between Langmuir's theory and Polanyi's theory are thus more apparent than real. The adsorption forces as well as Van der Waal forces have been shown to be of similar nature as homo-polar valency.

As for the effect of temperature, recently the theory of activated adsorption has been proposed by Taylor. This has been subsequently criticised by Steacie and Ward who attribute the change of adsorption to solvent effect while Burrage considers impurities to have marked effect on adsorption.

The second postulate of Langmuir (surface dissociation) explains the change of adsorption with temperature and the theoretical values obtained by the author indicates that the value of the number of dissociated atoms as well as the degree of dissociation may affect adsorption in a remarkable manner. Further experimental work on the measurement of specific surface, study of nature of the surface, and the variation of 'n' with temperature and pressure are required for clearing up the difficulties and obtaining a true picture of adsorption.

### 133. Adsorption of benzoic acid from mixtures of polar and non-polar liquids.

P. G. DESAI, Bombay.

The adsorption of benzoic acid by animal charcoal from three types of the following binary mixtures was determined :—

- (1) When both the components are non-polar.
- (2) When one component is polar and the other non-polar.
- (3) When both the components are polar.

It has been found that in case (1) the adsorption-composition curves are almost straight lines while in the two remaining cases, minima are generally obtained on the adsorption-composition curves. In the mixtures studied, no case is known where a maximum is obtained on the adsorption-composition curves.

It has been shown that in most cases, where maxima are obtained on the solubility-composition curves, minima are obtained on the adsorption-composition curves.

### 134. Adsorption of benzoic acid from polar and non-polar liquids.

P. G. DESAI, Bombay.

The adsorption of benzoic acid by animal charcoal, zinc oxide, aluminium oxide and fuller's earth from polar and non-polar liquids was determined.

It is found that the adsorption by zinc oxide was the greatest, while that by fuller's earth was the least. It is also found that adsorption from non-polar liquids is greater than that from polar liquids. It is shown that an inverse relation exists between solubility and adsorption.

### 135. Effect of polar and non-polar solvents on the solubilities of cinnamic, phthalic and succinic acids.

P. G. DESAI, Bombay.

The solubilities of the three acids differing greatly in their polar character were determined in a number of polar and non-polar solvents.

It is found that the solubilities of the acids in the non-polar and slightly polar solvents are in agreement with the polar nature of the solutes. With highly polar solutes like the phthalic and succinic acids,



their solubilities in the non-polar solvents are negligible while the solubility of the less polar cinnamic acid is appreciable in the same solvents. The solubilities in the more polar alcohols were not in agreement with the polar character of the solutes.

136. Solubilities of benzoic and salicylic acids in mixtures of organic solvents.

P. G. DESAI, Bombay.

In continuation of the work (*Proceedings Indian Science Congress, 1932, Section of Chemistry*), the solubilities of the two acids were determined in some more binary mixtures. It is found that when both the components of the mixture are non-polar, the solubility composition curves are almost straight lines, whereas in the case of a mixture of chloroform with non-polar liquids, the solubility-composition curves were convex towards the composition axis. With mixtures of alcohols with non-polar solvents and nitrobenzene, the solubility increases with the addition of alcohols, reaches a maximum and then decreases. The same was found with mixtures of nitrobenzene with the non-polar liquids.

137. Viscosity of sulphuric acid solutions and hydrate formation.

BALBHADRA PRASAD, Cuttuck.

Viscosity of sulphuric acid solutions is measured at a number of concentrations. The results are shown graphically and in tabular forms. In one graph, viscosity is plotted against concentration, and in another, the rate of variation of viscosity with concentration against the corresponding concentrations. From these two graphs the existence of four hydrates: trisulphuric monohydrate, and monosulphuric half-hydrate, monohydrate and dihydrate is derived. The possible electronic configurations of the hydrates have also been suggested.

138. A critical examination of the various empirical formulæ connecting viscosity, temperature and density.

BALBHADRA PRASAD, Cuttuck.

Various formulæ have been suggested connecting the viscosity of liquids with temperature and with density by various workers. The way in which viscosity, density, and absolute temperature are connected depends on a number of factors, e.g. molecular weight, the kind of linkages in the molecule, etc. No formula is satisfactory for a number of liquids. Even in the homologous series the formula for every liquid has to be slightly different.

139. Velocity of reactions in heterogeneous systems.

D. D. KARVÉ and K. K. DOLE, Poona.

Reaction velocities in heterogeneous systems are expected to depend on a number of factors, chief among them being the extent of the surface of contact between the phases and the velocity of the diffusion of the products of reaction from these surfaces into the interior of the phases. The reaction chosen for the study of velocity was that between carbon disulphide and caustic soda in different concentrations.

If the chief product of the reaction, viz. the thiocarbonate is oxidised off as soon as it is formed, the result would be practically the same as that of diffusion into the interior of the aqueous phase. This is brought about by the addition of hydrogen peroxide and the addition of varying quantities of this substance to the reaction mixture increases the velocity in proportion to the amount and concentration.



140. On the wave statistical theory of the mechanism of chemical reactions. I.—Unimolecular reactions.

A. GANGULI, Chandernagore.

By extending a method due to Kar and the author, applied to the case of radioactive disintegration, damped wave equations have been obtained for the phase space in the configuration of the original reacting substance and introducing a potential barrier, the following expressions for the velocity coefficient have been derived

$$k_1 = \frac{.91}{h} \sqrt{A(A-Q)} \cdot e^{-\frac{A}{kT}} \quad \text{(First approximation) } \dots\dots(1)$$

$$k_1 = e^{\beta \frac{(Q-A)}{\sqrt{A}}} \cdot e^{-\frac{A}{RT}} \quad \text{(Large damping) } \dots\dots\dots(2)$$

$$k_1 = c \frac{\sqrt{A(A-Q)}}{h} e^{k \sqrt{A} (U+Q-2A)} e^{-\frac{A}{kT}} \quad \text{(Small damping) } \dots\dots\dots(3)$$

Here  $Q$  is the heat of reaction, ' $A$ ' is the 'heat of activation' or the energy required to bring the molecules to a state, such that the spontaneous damping (as in the case of radioactive decomposition) may take place, or in the language of quantum mechanics, the resonance energy such that the 'anstauch' may take place between the configuration in which the molecules are present as an entity and that in which the resultant products are loosely held. In fact ' $A$ ' then becomes identified with the internal energy of the undecomposed molecules which again is equal to that of the system in which the resultant products are loosely held.  $\beta$  and  $k$  are factors involving  $A$ ,  $Q$ , and  $l$  the minimum distance at which attraction between the two components may exist. For  $Q=0$  Equation (1) reduces to an expression similar to that obtained before by Dushman, Polanyi, and Wigner, and the author. Equation (2) is similar to that obtained by Roginsky and Rosenkewitch from wave mechanics. The variation of  $k$ , at very low pressure is accounted for as due to change in  $l$  and also the damping coefficient, since this last is affected when the density is very small. A mechanism of activation is discussed.

141. The effect of salts, emulsoids, colloids, and some organic substances on the action of diastase on starch.

P. S. VARMA and SHEONATH PRASAD, Benares.

The results obtained by the previous workers on the effect of salts on the action of diastase on starch are conflicting. Attempts have been made to study the effect of the substances mentioned above in a more systematic manner under similar experimental conditions. In certain cases, the action of diastase is increased very considerably whereas in others it is either retarded very appreciably or inhibited altogether. In the case of certain salts, the strength of the solutions of the salts used has also a considerable influence. With aluminium chloride, for example, there is almost inhibition by N/10 solution, whereas there is a considerable activation by N/100 solution.



## 142. Esterification equilibrium in the vapour phase.

R. V. VALVEKAR and S. K. KULKARNI JATKAR, Bangalore.

In a previous communication it was shown that the equilibrium conversion of an equimolecular mixture of ethyl alcohol and acetic acid was 75 per cent. at 230° using potash alum and silica gel as catalysts. This work has been continued in order to find the temperature coefficient of the equilibrium constant. With equal rates of flow, ferric alum, phosphoric acid, sodium hydrogen sulphate, potassium hydrogen sulphate, silica gel alone and with 10 per cent. zirconium oxide and activated carbon gave at 150°, 5, 75, 40, 80, 50, 38 and 75 per cent. conversions respectively. The conversion with potassium hydrogen sulphate as the catalyst did not increase with reduction of rate. The result was confirmed by approaching the equilibrium from both directions.

## 143. The influence of Ni-Th-Ce promoters on the catalytic activity of Fe-Cu catalyst, supported on asbestos (Fe : Cu :: 4 : 1) in the synthesis of petroleum hydrocarbons from water-gas at ordinary pressure.

J. C. GHOSH and SUKUMAR SEN, Dacca.

It was found that the Fe-Cu catalyst of Fischer could be improved by using Ni as promoter. The best results were obtained with a catalyst of the composition Fe-Cu-Ni (4 : 1 : .22) containing traces of Th and Ce (Ni : Th : Ce :: 8 : .95 : .13) when, at 250°C. at a rate of passage of 10 c.c. per minute over 10 c.c. of catalyst material, a conversion of 21% by weight of the reacting gases was obtained at a single passage without any deposition of C.

Experimental data for a continuous experiment extending over 14 hours are given below :—

Wt. of water-gas passed over catalyst 5.49 gms.	Wt. of hydrocarbon obtained 1.14 gms.	Heat of combustion of reaction products 23,500 cal.
Heat of combustion 16,100 cal.	Theoretical yield of hydrocarbon :—1.3 grams.	

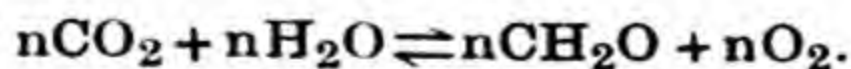
By following the reaction quantitatively it was found that there was always a periodic variation of the unsaturated-hydrocarbon-content of the effluent gases and under certain conditions of their other constituents as well.

## 144. Influence of temperature and light intensity on photosynthesis and respiration.

N. R. DHAR, Allahabad.

1. The Arrhenius relation connecting velocity and temperature of a reaction which is applicable to ordinary chemical reactions, is not valid in the case of the influence of temperature on photosynthesis in plants. The non-applicability of the Arrhenius relation to photosynthesis and many other phenomena in plant life can be explained from the following considerations :—

(a) It appears that in plant life, the following opposing reactions are taking place :—



The direct action (photosynthesis) is being opposed by the reverse reaction (respiration) which increases according to the law of mass action with increase in the concentration of carbohydrates formed from photosynthesis.



(b) There is reason to believe that the velocity of respiration in plants is appreciably accelerated by light.

(c) The influence of temperature on respiration appears to be greater than that on photosynthesis.

2. The greater influence of temperature on photosynthesis in presence of strong light than that in weak light can be explained from the foregoing considerations. Hence, it is needless to assume that there are two reactions involved in photosynthesis.

3. The observations of Willstätter and Stoll that leaves of low chlorophyll-content show a lower acceleration of photosynthesis with increase in temperature than the leaves of high chlorophyll-content have also been explained from the same point of view.

4. The experiments of Willstätter and Stoll showing that in chlorophyll-rich leaves an increase of light intensity does not affect photosynthesis have been explained from the view-point of 'exhaustion effect' as observed in ordinary photochemical reactions.

5. That oxygen is essential for photosynthesis appears to be due to the fact that plant life depends on oxygen respiration and the activity of the plant and along with it its photosynthetic power depend on its respiratory activity.

6. The photosynthetic activity is exceedingly high in young leaves and is not proportional to the chlorophyll-content. This is because the respiratory activity of young leaves is very high. In plant life, as well as in animal life, metabolism decreases with age.

7. In plant life in the absence of iron compounds, respiration and photosynthesis become defective as in chlorotic plants, because iron compounds accelerate respiration.

8. In the animal world, the length of life depends inversely as the rate of living. The duration of the catalytic activity of an active catalyst appears to be short. These considerations are applicable to plant life as well.

9. The phenomenon of 'solarisation', that is, the disappearance of carbohydrates formed from photosynthesis after prolonged illumination appears to be due to respiration, that is, their oxidation by oxygen in presence of light. The respiration, that is, the oxidation of carbohydrates is also increased by increase of temperature caused by light absorption.

10. The compensation point, that is, the light intensity at which the photosynthetic and respiratory activity of plants compensates each other, decreases with decrease of temperature.

11. Respiration appears to be the more fundamental reaction in plant and is more important to plant life than photosynthesis which predominates in plants only under restricted conditions of temperature and light intensity.

#### 145. Formaldehyde in rain water.

N. R. DHAR and ATMA RAM, Allahabad.

1. It has been observed that freshly collected rain water contains formaldehyde to the extent of 0.001 to 0.00015 grams per litre.

2. The amount of formaldehyde in rain water increases if the rain is preceded by bright sunny days. When the days are cloudy and there are frequent showers, the amount of formaldehyde decreases and may be altogether absent immediately after a very heavy shower.

3. The rain water should be immediately analysed when collected, because a part of the formaldehyde is lost by vaporisation and another part by polymerisation.

4. It is believed that the formaldehyde in rain water is formed by the combination of carbon dioxide and water vapour present in the atmosphere by the absorption of ultra-violet light from the sun.



5. Formaldehyde in rain water cannot be due to the photo-decomposition of substances of vegetable origin.

6. Formaldehyde vapour shows a light absorption between 3700 and 2500  $\text{\AA}$ , the maximum absorption being at 2935  $\text{\AA}$ , characteristic of aldehydes. It appears that not only ozone absorbs radiations of short wavelengths from the sun, but the formaldehyde present in the atmosphere also absorbs solar ultra-violet radiations.

7. It appears that the water molecules are decomposed by absorption of short-wave radiations and the hydrogen atoms set free reduce carbon dioxide to formaldehyde, which may be formed in the atmosphere at heights less than those where ozone is generated.

#### 146. Formation of periodic precipitates in the complete absence of gels.

N. R. DHAR and R. N. MITTRA, Allahabad.

In a recent note to *Nature*, it was reported that periodic precipitates are obtained in the coagulation of sols of ferric, chromic, and stannic hydroxides by electrolytes. The authors have now obtained similar periodic precipitates with sols of ceric, zirconium, thorium hydroxides and vanadic acid and ferric arsenate when coagulated by univalent electrolytes. For obtaining this periodicity, the sols must be fairly pure and the velocity of coagulation low. The authors have determined the adsorption of the hydroxide sols by their respective hydroxides in the precipitated condition, and have observed that when the sols are fairly pure they are markedly adsorbed by their precipitates. These results on Liesegang ring formation obtained in the complete absence of a gel or a foreign medium are due to the adsorption of the sols by their precipitates. Hence, in order to obtain Liesegang rings, it is necessary that the sol and its precipitate should co-exist for a sufficiently long time. All these results are easily explained from the theory of Liesegang ring formation advanced by Dhar and Chatterji in 1924.

#### 147. Constitution of iodic acid and potassium iodate.

M. R. NAYAR and TOTA RAM GAIROLA, Lucknow.

From precipitation values of colloidal solutions by means of electrolytes Dhar and co-workers found that iodate ion probably was bivalent. (Dhar, *J. Ind. Chem. Soc.*, 1928, p. 591; *ibid.*, 1932, p. 322.) They have attempted to solve the problem by three methods :—

- (1) Ostwald's conductivity method.
- (2) Electrometric titration of  $\text{HIO}_3$  with  $\text{NaOH}$  by means of an oxygen electrode.
- (3) Determination of Van't Hoff factor from freezing point depression of  $\text{KIO}_3$  solution.

All the three methods give indications that iodates in solution contain only two ions and that iodic acid is probably mono-basic.

#### 148. Studies on crystallisation and super-saturation.

M. R. NAYAR and L. N. SRIVASTAVA, Lucknow.

In continuation of the work reported before the *Academy of Sciences*, U.P. (*Proceedings*, Vol. I, Dec. 1931), the authors have determined the supersolubility curve for oxalic acid in water, and the curves for other substances are being obtained.



149. Study on the arsenic content of the sandalwood and oil derived from trees treated with arsenical solutions.

A. V. VARADARAJA IYENGAR, Bangalore.

It has been shown by the author elsewhere that a very strong solution of arsenic kills effectively diseased sandal plants. In view of the fact that the heartwood and oil from sandal trees are used in medicine and industry, it was desirable to know whether arsenic passed into the heartwood and also into the oil. For this purpose, the heartwood from treated trees was digested with a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  in the proportion of 7 : 3 and after complete removal of nitrous fumes, the residue was tested for arsenic by the Gutzeit method. It was found that the heartwood contained arsenic as  $\text{As}_2\text{O}_3$  to the extent of 0.00006% to 0.00002% and in a few cases no trace of arsenic could be detected.

The oil was extracted by the solvent method, digested and tested for arsenic by the method detailed above, with the result that no arsenic could be detected. The extraction has been carried out by the steam distillation method and the oil is being tested for its arsenic content.

150. Dilatometric studies in enzyme action. Part III.—Glucosides.

H. B. SREERANGACHAR and M. SREENIVASAYA, Bangalore.

A dilatometric study of the enzyme hydrolysis of three glucosides, amygdalin, arbutin, and salicin has been made by means of the dilatometer described before (*J. Indian Inst. Sci.*, 13 A, 1932).

The amount of reducing sugar liberated in a given period is proportional to the volume change occurring in the dilatometer. The contraction constant per grammolecule of the glucoside is calculated from the observed depression and the corresponding amount of glucoside hydrolysed.

Emulsin-salicin system gives a contraction constant of 4.10. In the case of emulsin-amygdalin and emulsin-arbutin however no volume change is observed during hydrolysis.

The significance of these results is discussed.

151. Dilatometric studies in enzyme action. Part IV.—Polysaccharides.

H. B. SREERANGACHAR and M. SREENIVASAYA, Bangalore.

The hydrolysis of the two colloidal polysaccharides, starch and glycogen, by four different diastases, pancreatin, ptyalin, malt diastase, and taka-diastase has been investigated in the dilatometer. The contraction constants of the reaction are calculated on 100 gms. of the substrate.

	Pancreatin.	Ptyalin.	Malt diastase.	Taka-diastase.
Starch ..	0.68	0.675	0.79	1.57
Glycogen ..	0.45	0.83	0.54	1.47

The constants tabulated above reveal that starch is hydrolysed by pancreatin and ptyalin to very nearly the same extent while malt and taka-diastases carry on the reaction to a further stage, the taka-diastase



bringing about the maximum hydrolysis. In the case of glycogen-hydrolysis also, pancreatin gives the least and taka-diastase the highest depression.

In every case the reaction has been followed by an entirely independent chemical method involving the estimation of the reducing sugars released during the hydrolysis. It is therefore possible to correlate the total depression with the amount of sugar liberated and arrive at a constant which has a relation to a grammolecule of sugar.

## 152. Dilatometric studies in enzyme action. Part V.— Estimation of urea and arginine.

H. B. SREERANGACHAR and M. SREENIVASAYA, Bangalore.

Changes in volume which accompany enzyme reactions are proportional to the amount of substrate hydrolysed. The  $\alpha$  contraction constants of enzyme-substrate systems which can be determined are useful in the estimation of substrates in physiological fluids. The contraction constants of urease-urea and arginase-arginine which have been found to be 24.13 and 5.02 respectively have been utilised for the estimation of urea in urine and arginine in gelatin and casein hydrolysates.

	Urea in 1 litre of urine.		Percentage of arginine in.	
	Urine No. 1.	Urine No. 2.	Gelatin.	Casein.
	gms.	gms.		
Dilatometric method ..	6.085	5.82	7.95	3.52
Chemical method ..	6.317	5.94	7.8	3.33

The results of dilatometric estimation as well as those by chemical methods of estimation are in fair agreement.

## 153. Dilatometric studies in enzyme action. Part VI.— Kinetics and contraction constants of Inulin-Inulase system.

N. KESHAVA IYENGAR and M. SREENIVASAYA, Bangalore.

The kinetics of inulase have been investigated in the dilatometer and also followed chemically by periodic estimations of the fructose produced during the reaction. The two sets of results reveal a definite proportionality of the dilatometric depressions with the amounts of sugar liberated. The contraction constant which has been calculated per 100 grams of the substrate is found to be 3.65. When expressed on the basis of a grammolecule of sugar produced, the contraction constant attains a value of 7.1.

## 154. Dilatometric studies in enzyme action. Part VII.— Hydrolysis of glycine anhydride.

M. SREENIVASAN and M. SREENIVASAYA, Bangalore.

The hydrolysis of glycine anhydride to the corresponding dipeptide and the dipeptide to two molecules of glycine has been followed in the



dilatometer. The first reaction involving the fission of the di-keto-piperazine ring, is brought about by dilute (N/10) alkali and is accompanied by a rise in the dilatometric column. The reaction reaches an equilibrium in about 10 to 12 hours, after which the reaction mixture is analysed for the free amino-nitrogen which gives a measure of the dipeptide produced. The observed dilatometric elevation is proportional to the amount of the anhydride hydrolysed and therefore the elevation constant per grammolecule of the anhydride can be calculated. In the case of di-keto-piperazine the elevation constant is found to be 7.6.

The hydrolysis of the dipeptide is being followed by enzymes in the dilatometer to determine the constant for the second stage of the reaction.

155. Studies in the resistance of sandal plants to spike disease.  
Part III.—Nitrogenous constituents.

Y. V. SREENIVASA RAO and M. SREENIVASAYA, Bangalore.

In a preceding communication (*Indian Science Congress Abstracts*, 1931, *Section of Chemistry*) it was pointed out that leguminous hosts in general render the parasitic sandal plant particularly susceptible. The chemical factors which influence susceptibility and resistance to disease have now been investigated particularly with reference to the nitrogenous constituents, some of which appear to encourage the rapid multiplication and increase the virulence of the infective principle.

Susceptible sandal plants nourished by hosts like *Acaria farnesiana* are characterised by a high content of basic nitrogen while those fed by hosts like *Margosa*, *Rutea graveolens* contain a high percentage of the non-basic fraction.

Form of Nitrogen.	Results expressed on percentage total water soluble nitrogen.	
	Susceptible sandal.	Resistant sandal.
Basic ..	16.78	6.4
Non-basic ..	70.00	90.0

A detailed analysis of the nature of basic and non-basic fractions is in progress.

156. Contributions to the study of spike disease of sandal.  
Part IV.—Studies in the resistance of sandal to spike.

M. SREENIVASAYA and M. SRINIVASAN, Bangalore.

Among the various factors known to influence disease-resistance in plants, the hydrogen ion concentration and buffering capacity play an important rôle. These two factors have been investigated with sandal plants which have been cultured in pots under controlled conditions and in association with known host plants. The buffering capacity of the tissue fluids has been determined not only with reference to the addition of alkali but also to the addition of acids. The significance of determining the buffering capacity of tissue fluids to addition of acids is realised, if attention is called to the fact that with the onset of disease, acids accumulate in the plant and favour the growth of the infective principle.



The hydrogen ion concentration and buffering capacity of various tissues of the plant, leaf, root, bark, and wood have been separately determined with a view to locate the region of maximum and significant change with respect to the above two factors. In general, the tissue fluids of the spiked plant possess a higher buffering value with respect to either acid or alkali. This can be correlated with the increase in the amino-nitrogen occurring with the onset of disease. The maximum change in the buffering capacity is found to occur in the root. The results are given in the following table:—

			pH.	Volume of titre to shift pH by unity for 2 c.c. of sap.	
				Acetic acid N 10 c.c.	NaOH N/10 c.c.
Leaf	{ Healthy ..	..	5.4	3.0	0.6
	{ Spiked ..	..	5.0	6.0	0.7
Root	{ Healthy ..	..	5.9	0.4	0.1
	{ Spiked ..	..	5.3	3.0	0.3
Bark	{ Healthy ..	..	5.0	3.0	0.3
	{ Spiked ..	..	4.9	5.5	0.5
Wood	{ Healthy ..	..	5.8	0.8	0.3
	{ Spiked ..	..	5.2	2.0	0.3

157. Contributions to the study of spike disease of sandal.  
Part V.—Respiratory activity of diseased and healthy tissues and tissue fluids.

N. KESHA VA IYENGAR and M. SREENIVASAYA, Bangalore.

A respiration study of the healthy and diseased tissues and tissue fluids of sandal has been made employing the Barcroft differential respirometer with modifications introduced by Dixon and Elliot (*Biochem. J.*, 1930) for quick and efficient CO<sub>2</sub> absorption. Healthy tissues and tissue fluids produce twice as much carbon dioxide as that generated by corresponding diseased materials. This significant result accounts for the accumulation of the products of incomplete combustion—the organic acids. The respiratory activity of healthy and diseased leaves at different stages of growth and after treatment with liquid air, has been made.

158. On Inulase. Part II.—Methods of purification.

N. KESHA VA IYENGAR and M. SREENIVASAYA, Bangalore.

Inulase from *Aspergillus* cultured on an aqueous extract of artichoke, is associated with other carbohydrases, more particularly with invertase which occurs in considerable quantity. 1 c.c. of the extract acting upon 5 c.c. of 0.5 per cent. sucrose produces 15.5 mgms. of reducing sugar (calculated as glucose). Purification of the inulase extract, therefore, amounted practically to an elimination of the accompanying invertase and the adsorption method recommended by Pringsheim was followed. Calcium hydrogen phosphate exhibits a preferential adsorption for inulase which could be eluted out by citrate buffer at 3.8 pH. Sorensen's phosphate buffer at 6.8 pH was, however, found to be a more efficient elutant. Repeated adsorptions and elutions increase the purity of inulase but



bring about a loss in the activity of the resulting extract either due to material losses of the enzyme or inactivation or both.

Aluminium and zirconium hydroxides were found to adsorb both the enzymes from the extracts quantitatively and this fact could be utilised for a preliminary purification to eliminate the inert solids associated with the extract.

Short period dialysis (48 hrs.) of the extract in parchment thimbles against a stream of distilled water shows that invertase passes out more quickly than inulase. Continued dialysis for 5 days results in complete passage of both the enzymes.

#### 159. Chemical examination of the seeds of *Pongamia Glabra*.

M. C. TUMMIN KATTI, Bangalore.

During the course of the complete analysis of the seeds with a view to find out the nature of the active principle responsible for the curative properties of the *hongay* oil three crystalline compounds in addition to *Karanjin*, have been isolated and their properties described. The active principle appears to be a viscous non-saponifiable resinous matter. Other constituents isolated from the seeds, are fatty acids, phytosterol, and a large amount of sucrose. Clinical trials of the non-saponifiable resinous matter on a number of cases of skin diseases have confirmed the therapeutic activity of the oil.

#### 160. A preliminary study on the cultivation of *Datura Stramonium*.

M. C. TUMMIN KATTI, Bangalore.

In order to study the climatic effects on and the seasonal variations in the yield and the alkaloidal content of *D. stramonium* leaves, experiments with small plots (16 × 12 feet) have been conducted.

The results obtained so far indicate that removal of flower-buds, as they appear, not only increases the yield of leaves by more than 100 per cent., but also the alkaloidal content of the leaves from such plants increases by 30–40 per cent.

It is reported that sun-drying has a deleterious effect upon the quality of the drugs. The analysis of the leaves dried in the sun and in a hot air oven (40–50°C.) did not, however, indicate any difference in the alkaloidal content of the leaves.

#### 161. Indian aconites.

M. C. TUMMIN KATTI, Bangalore.

In order to see if any of the varieties of aconites growing in Kashmir could be substituted for the official aconite, *Aconitum napellus*, two samples of aconites, *A. heterophyllum* and *A. chasmanthum*, have been analysed as to their alkaloidal content. *A. heterophyllum* has been found to contain a small amount (0.047 per cent.) while *A. chasmanthum* contained nearly 7.0 per cent. of ether-soluble alkaloids. The principle alkaloid (Indaconitine) from *A. chasmanthum* is not identical with aconite but has got very similar chemical and physiological properties.

The tincture of *A. chasmanthum* when fresh is found to be physiologically 13–14 times as active as a fresh tincture of *A. napellus*.

Just like the official tincture (Tincture, Aconite, B.P.), the tincture prepared from *A. chasmanthum* also deteriorates considerably in its physiological action on storage. The rate of deterioration with respect to time has been studied and the results described.



162. Chemical examination of the Rhizomes of *Rheum emodi*.

M. C. TUMMIN KATTI and GHOUSE MOHIYUDDIN, Bangalore.

During the course of the complete analysis of Indian Rhubarb, a number of compounds have been isolated. In addition to fatty acids and phytosterol, chrysophanic acid, frangula-emodin, rhein, a mixture of anthraquinone glucosides which on hydrolysis yielded chrysophanic acid and another glucoside-rhaponticin in considerable amounts have been isolated and identified.

163. Proteins of *Phaseolus mungo*.

H. JAI RAM, Bangalore.

The globulins from this legume have been obtained and fractionated into two distinct chemical entities differing from each other both in their content of nitrogen and sulphur. A very interesting feature is the existence in these globulins, of phosphorus which could not be eliminated in spite of repeated purification and evidence has also been obtained to show that it is in organic combination. The amount of phosphorus contained in any one of the fractions is constant for the particular globulin but the two differ very widely in their phosphorus contents. Further work is in progress to study the biological value of the individual proteins and the nature of the phosphorus linkage involved in the phosphoproteins.

## 164. The mechanism of synthesis of proteins in plants.

K. S. VARADACHAR, Bangalore.

In the previous years (*Proceedings of the Indian Science Congress, Section of Chemistry*, 1931 and 1932) experiments were reported on the injection of nitrogen-starved sunflower plants (*Helianthus annuus* Linn) with potassium nitrate solution and on studies of the changes undergone by the absorbed nitrate. In the present paper the author has studied sampling the injected plants every two hours, day and night, and analysing the samples for nitrogen distribution. The Hassmann numbers are discussed in their correlation to the synthesis of protein in plants. There is evidence to suggest that the high percentage of humin fraction observed (sometimes as high as 20 per cent. of the total N) is due to certain seasonal variations. Further experiments are in progress.

165. The pigment of the flowers of *Tagetes erecta*.

H. S. MAHAL and K. VENKATARAMAN, Lahore.

The yellow colouring matter of the flowers of *Tagetes erecta* (Hindi and Bengalee, Ganda; English, the French marigold) has been isolated and identified as the known quercetagenin, 3 : 5 : 6 : 7 : 3' : 4'-hexa-hydroxy-flavone.

## 166. Chemical investigation of Indian medicinal plants.

Part I.—Preliminary chemical examination of the root bark of *Capparis Horrida*.

S. N. CHAKRAVARTI and A. VENKATASUBBAN, Chidambaram, Madras.

A systematic analysis of the root bark, which is used as a cure for Cholera and as a sedative, stomachic, and anti-idriotic, has been made. The active principle of the root-bark is an alkaloid which has been isolated. The physiological and pharmacological action as well as the composition and the constitution of this alkaloid are under investigation.



167. Chemical investigation of Indian medicinal plants. Part II.—Preliminary chemical examination of the leaves of *Pithecolobium Bigeminum*.

S. N. CHAKRAVARTI and KRISHNAMURTI GANAPATI,  
Chidambaram, Madras.

A systematic analysis of the leaves of *Pithecolobium Bigeminum*, which is used as a cure for leprosy and also as a stimulant to promote the growth of hair, has been made, which shows that the active principle of the leaves is a mixture of acids, one of which is easily soluble in water but not in alcohol, whilst the other is readily soluble in alcohol but not in water. Alkaloids, glucosides, tannins, etc., were found absent.

168. Colouring constituents of alkanet root. Part II.—Composition and derivatives of Anchusin.

D. N. MAJUMDAR and G. C. CHAKRAVARTI, Bangalore.

The ether extract of the root from which alkannin has been removed previously, gives about a 25 per cent. yield of the second colouring matter, anchusin. It gives a potassium and a barium compound of the formulae  $C_{30}H_{34}O_9K_2$  and  $(C_{30}H_{34}O_9K)_2Ba$  respectively. The molecular weight of some simple derivatives also support the formula  $C_{30}H_{36}O_9$  for anchusin.

A number of derivatives,  $C_{30}H_{32}O_9(COCH_3)_4$ ;  $C_{30}H_{31}O_9(COCH_3)_5$ ;  $C_{30}H_{34}O_7(OCH_3)_2$ ;  $C_{30}H_{32}O_7(OCH_3)_2(COCH_3)_2$ ;  $C_{30}H_{32}O_9(CO.C_6H_5)_4$ ;  $C_{30}H_{32}O_9Br_4$  and  $C_{30}H_{30}O_9Br_6$  have been obtained.

Oxidation with nitric acid gives different products which are some complex nitro-carboxylic acids together with simple acids like oxalic acid and succinic acid.

169. Colouring constituents of alkanet root. Part III.—Isolation of a new colouring matter.

D. N. MAJUMDAR and G. C. CHAKRAVARTI, Bangalore.

The residue of the root after exhaustive extraction with ether gives a third colouring matter for which the name alkanninin is proposed. The method of its isolation and purification is described in detail. Some simple derivatives have been prepared for finding out its composition.

170. Isolation of  $\beta$ -naphthylamine from coal tar.

S. K. GANGULY and P. C. GUHA, Bangalore.

Though a number of bases have been isolated from coal tar, no mention is made in the literature about the existence of  $\beta$ -naphthylamine. Anthracene oil (b.p.  $270^\circ$ – $350^\circ$ , Sp. Gr. at  $25^\circ$ , 1.0310) is extracted with hydrochloric acid, the acid extract, steam-distilled and the bases, precipitated with caustic soda, subjected to fractional distillation. The fraction coming over between  $190^\circ$ – $245^\circ$  at 30 mm. is treated with warm sulphuric acid (1 : 5) and on cooling the insoluble sulphate of the amino-base separates out as a solid which on being boiled with 10 per cent. caustic soda solution yields  $\beta$ -naphthylamine as white shining crystalline plates. After crystallisations from water it melts at  $112^\circ$ , yield 0.56 per cent. in this fraction. Identity has been confirmed by taking mixed melting point with a genuine sample and also from combustion results.



171. Examination of the Phenol and Cresol contents in the carbolic oil manufactured by Bengal Chemical and Pharmaceutical Works from Calcutta Gas Works tar.

S. K. GANGULY and P. C. GUHA, Bangalore.

The middle oil (b.p.  $170^{\circ}$ – $230^{\circ}$ ; Sp. Gr. at  $25^{\circ}$ , 0.9876) contains tar acids to the extent of 30 per cent., bases 2.6 per cent., and neutral oils 67.4 per cent. The tar acids are repeatedly fractionated with fractionating columns under standard conditions, with necessary corrections of temperature due to variation of pressure. The phenol content found in the fraction up to  $180^{\circ}$  by 'Crystallisation point method'—5.7 per cent.; ortho-cresol (b.p.  $187^{\circ}$ )—11.98 per cent.; meta-cresol estimated as trinitro-compound (*Z. Angew. Chem.*, 1900, 13, 759)—2.17 per cent.; para-cresol and other higher acids of the series—10.15 per cent.

172. Chemical investigation of the high boiling bases of anthracene oil (B.p.  $170^{\circ}$ – $350^{\circ}$ ).

S. K. GANGULI and P. C. GUHA, Bangalore.

Excepting the isolation of some high boiling bases like di-methyl-quinolines and acridine in the high-boiling fractions of the bases obtained from coal-tar, no work appears to have been done on the isolation of the bases occurring in anthracene oil. The high-boiling bases show sign of decomposition when subjected to ordinary process of distillation. Their separation has been tried by fractional distillation under highly reduced pressure, viz. 2-3 mm. Fourteen fractions, each distilling within a range of five degrees from  $85^{\circ}$ – $155^{\circ}$ , have been collected and their specific gravity, refractive index, and average composition studied to form an approximate idea about their composition.

Attempts for the isolation of individual carboxylic acids by oxidising the alkyl groups (*Ber.*, 1889, 22, 267) of the mixed bases have not been successful due to the fact that the mixture of acids is obtained only as a semi-solid viscous mass. Isolation of three individual solid esters melting respectively at  $208^{\circ}$ ,  $201^{\circ}$  and  $101^{\circ}$  ( $R\text{-COO}\cdot\text{CH}_2\text{-CO}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$ ) has been effected.

173. On the problem of identity of jute and cotton celluloses.

J. K. CHOWDHURY and N. N. BOSE, Dacca.

The standard celluloses prepared from cotton and jute were subjected to different chemical treatments. The degree of acetylation and yield of the acetylated product, yield of methyl-glucoside and of crystalline glucose, yield of cellobiose-octacetate, yield and methoxyl content of methylated cellulose—all gave identical results with both the celluloses. The viscose reaction, surface tension of viscose solutions and viscosity of solutions of cellulose and its carefully prepared derivatives, however, indicated wide difference in the case of the two celluloses. It is suggested that both the celluloses consist of glucose units only, combined together in a similar manner. The number of glucose units is however different in the two cases—cotton cellulose consisting of a larger number of glucose units than jute cellulose.

174. 'On the preparation of pure cellulose from jute fibre.

J. K. CHOWDHURY and N. N. BOSE, Dacca.

Cotton cellulose prepared by the method of Correy and Grey without the use of bleaching agents and treated with 17.5% alkali in the cold was used as a standard for the comparison of purity. Jute fibre, delignified by chlorine peroxide method, was extracted with hot water and then



alternately treated with boiling 5% alkali and cold 17% caustic soda several times. In ash content, furfural value and solubility in 17% alkali, this jute cellulose was found to have identical values with the standard cotton cellulose. Lignin, urenic acid, fat, and resin were found absent in both the celluloses.

### 175. Jute-leaves—*Corchorus Capsularis*. Part I.—Their chemical composition.

N. K. SEN, Dacca.

The present investigation forms a systematic analysis of the various substances present in the jute-leaves. The leaves of *Corchorus Capsularis* were extracted successively with the following solvents:—

			Per cent. of extract.
Petroleum ether (b.p. 40°–50°)	..	..	9.80
Ethyl ether	..	..	2.01
Chloroform	..	..	1.73
Alcohol (95%)	..	..	12.26
Water	..	..	7.35
	Residue	..	63.25
	Loss	..	3.60
Total			100.00

The light petroleum extracted a vegetable wax and essential oil, ether, chlorophyll and a small quantity of a crystalline solid of phenolic character, the chloroform, a trace of bitter principle and the alcohol, most of the bitter principle and of tannin but no alkaloids, the water extracted reducing carbohydrates and inorganic salts mainly potassium chloride.

From the alcoholic extract of the jute-leaf a bitter substance was isolated as white amorphous powder which is identical with Capsularin isolated by Saha and Choudhury (*J. Chem. Soc.*, 1922, 121, 1044). It also bears a close relationship with Corchorin isolated from jute seeds by the author (*Indian Science Congress*, 1930). Further work on the constitution of the bitter principle is in progress.

### 176. Pectins and hemicelluloses from some of the Indian fruits and vegetables.

H. S. SHARMA, Bangalore.

Investigations on the pectin contents of some of the Indian fruits and vegetables reveal that some of them are excellent commercial sources for pectin, which is extensively used in the manufacture of jams and jellies. Pectin was isolated from palm-fruit, chow-chow, turnips, gourd, and papaya. Gourd and papaya especially contain at certain stages of maturation, as much as 35 per cent. and 27 per cent. respectively of pectin, and therefore can be profitably used as commercial sources. Some of these pectins when precipitated with acetone and ethyl alcohol, give fractions whose chemical nature is under investigation. The pectin from papaya when refluxed with dilute alkalies, changes into a product whose properties are very similar to those of the hemicellulose obtained directly from raw materials. Further evidence of the degradation of pectin to hemicelluloses is being obtained by similar treatment of pectin from other sources.

Investigations on the inter-relationship of sugars, pectins, hemicelluloses, celluloses, and lignins are in progress.



177. Physiological products of the lac insect. Part I.—The nitrogenous constituents of the body and fluid.

N. K. RANGA RAO *and* M. SREENIVASAYA, Bangalore.

Lac-encrustation containing mature insects, three weeks prior to swarming, after mechanical separation from the green twigs, was ground with 1.0 per cent. sodium chloride solution. The blood red extract was centrifuged to eliminate fat and suspended particles. The clean deep red extract, on acidification gave a nitrogen value of 12.1 per cent. The filtrate, on saturation with salt, yields a flocculent precipitate (B), which can be recovered by centrifuging. The clear centrifugate containing all the lower serum-proteoses and poly-peptides represents the third fraction which was also subjected to Van Slyke analysis. A detailed study of the bases has been carried out by Kossel's silver-baryta method. The basic fraction amounts to about 50 per cent. of the total nitrogen and 25 per cent. represents the histidine fraction. The analytical data strongly points to the existence of a histoprotamine closely allied in composition to the protamine-like body isolated by Dunn from the testicles of *Sardina Coerula*. Further fraction of the serum-proteoses of the blood is under progress.

178. Shellac esters. Part I.

M. VENUGOPALAN *and* N. NARASIMHA MURTY, Namkum.

Attempts are made for preparing some shellac esters of glycerine and ethylene glycol with a view to improve the properties and increase the use of shellac in the various industries. Optimum conditions for the esterification process with regard to time and temperature of reaction, and the action of various inorganic catalysts have been studied. The different shellac esters prepared have been examined for such specific properties as colour, appearance, acid value, solubility in different solvents, resistance to water, effect of baking, etc. The use of these esters as possible substitutes for plasticisers and also as a medium for preparing some adhesive compositions have been suggested.

Esterification with beta-naphthol, resorcinol, pyrogallol, etc., did not yield esters of any appreciable reduction in acid value. The products obtained from these are hard and brittle but are greenish dark in colour.

Experiments in connection with the preparation and study of the properties of some mixed esters of shellac in combination with other natural and synthetic resins such as rosin, copa!, glytal, etc., are in progress. The use of these esters in the development of some oil-varnishes is also being studied.

179. Effect of plasticisers on shellac films.

M. RANGASWAMI, Namkum.

The effect of including a plasticiser in the composition of a shellac varnish on some of the properties of the resulting film has been investigated.

Working with pure unbleached shellac varnishes it has been found that no advantage will be gained by plasticising the film from the point of view of both the amount of water absorbed and the opacity of the film as a result of water absorption since plasticised films are as much affected by water as pure shellac films; plasticising will, nevertheless, improve the flexibility of the film to a certain extent as a result of which the film will much less readily crack when subjected to alternating conditions of extreme drought and humidity.



It has also been shown that the plasticisers will, to a small extent, increase the resistance of the film to scratching and abrasion but will not, however, prevent the films from cracking when subjected to the bending test.

#### 180. Electro-deposition of shellac.

N. NARASIMHA MURTY, Namkum.

The colloid chemical aspects of alkaline solutions of shellac are discussed. The experimental portion on the electro-deposition deals with the nature of the deposits obtained from (i) seed lac, (ii) ether-insoluble lac, (iii) ether-soluble lac, (iv) shellac. The influence of chlorine ion is found to be the greatest and that of acetate ion the least in obtaining a polymerised deposit. The alcohol-soluble portion of the polymerised deposit consists of ether-soluble lac, while the alcohol-insoluble portion of the deposit consists of ether-insoluble lac. These results are in accord with the observations made by Harries and Nagel in studying the effect of hydrochloric acid on the polymerisation of ether-insoluble portion of shellac. The scope of further work in connection with electro-deposition is indicated.

#### 181. Structure of *Psoralen*—one of the constituents of the seeds of *Psoralea Corylifolia* (Linn).

H. S. JOIS and B. L. MANJUNATH, Bangalore.

A small amount of solid material separated from the oil obtained by the extraction of the seeds of *Psoralea Corylifolia* with low boiling petroleum (yield 0.2 to 0.3 per cent. of the weight of the seeds). The substance was resolved into two constituents by repeated fractional crystallisations from various solvents. The main component,  $C_{11}H_8O_3$ , named *Psoralen* melted at  $163^\circ$  and the other at  $113^\circ$ . Both of them were found to be lactonic bodies.

*Psoralen* can be crystallised from water in long colourless needles, and possesses a distinct aromatic odour. The alkaline solution is reduced by means of sodium amalgam and *di-hydro-psoralic acid* is precipitated on acidification. This acid when distilled *in vacuo* gives *di-hydro-psoralen*,  $C_{11}H_8O_3$ . *Psoralen*, when treated with methyl sulphate, gave the *methyl-ester of methoxy-psoralic acid* from which the free acid could be obtained by saponification.

Evidence is adduced to indicate that *Psoralen* may be regarded as belonging to the class of Cumarino-Cumarones and is the parent substance of the *Bergapten* group.

Further detailed studies are in progress.

#### 182. The chemical examination of the roots of *Aristolochia Indica* (Linn). Part II.

B. L. MANJUNATH, S. SIDDAPPA, and S. VENKATA RAO, Bangalore.

The alcoholic extract of 75 Kg. of the roots was first subjected to steam distillation for obtaining the essential oil, the characteristics of which have been reported in a previous communication (*Indian Science Congress*, 1932).

This essential oil consisted principally of a sesquiterpene (b.p.  $121^\circ/10$  mm.), and a sesquiterpene alcohol (b.p.  $158^\circ/10$  mm.). A considerable quantity of a resin insoluble in alcohol separated after steam distillation. The aqueous layer on treatment with sodium carbonate gave a small amount of alkaloidal material. This was extracted with chloroform and the principal component was found to have the composition  $C_{24}H_{25}O_4N$  and melted at  $158.9^\circ$  with decomposition. The hydrochloride



decomposed at  $266^{\circ}$ . In addition to this a small amount of the hydrochloride of an alkaloid melting at  $310^{\circ}$  (0.3 g.) has been isolated. The free base from this was found to be difficultly soluble in most of the organic solvents.

The residue left after steam distillation was dissolved in alcohol and separated from resinous material, dried on the powdered roots and extracted successively with petroleum ether, ether, chloroform, ethyl acetate, and alcohol.

The petroleum extract gave 1.5 Kg. of a dark brown oil, from which a small amount of phytosterol glucoside separated out gradually. A detailed examination of the constituents of the oil is included in the paper. It is of interest to note that the unsaponifiable matter contained a large proportion of the sesquiterpene alcohol already referred to, and also a phytosterol melting at  $137^{\circ}$ .

A yellow crystalline bitter principle (m.p.  $276^{\circ}$ ) was isolated from the ether extract. The rest consisted mainly of resinous bodies. The ether extract also contained small amounts of basic material. A considerable proportion of the alkaloid occurring in the free state in the plant was obtained from the chloroform extract. The bitter principle was also recovered from the chloroform and ethyl acetate extracts. Further indications were obtained of the presence of glucosidic constituents mainly of the bitter principle in ethyl acetate and alcohol fractions. Further work is in progress.

### 183. Proteins of Fenugreek.

Y. V. SREENIVASA RAO and M. SREENIVASAYA, Bangalore.

With a 6 per cent. sodium chloride solution, 40 per cent. of the total nitrogen present in the Fenugreek powder can be extracted. On dialysis in fluted filters of parchment against a slow stream of distilled water for five days the salt extract gave a precipitate (A) the globulin, which can conveniently be recovered by centrifuging. On acidification the clear centrifugate yields a flocculent precipitate (B) which represents the albumin fraction of Fenugreek. A and B on analysis gave respectively the following percentages: Total nitrogen 17.2 and 15.9, Phosphorus 0.00 and 0.31, and Sulphur 0.14 and 0.29. The Van Slyke analysis of the two preparations A and B reveals that the globulin is characterised by a surprisingly high content of histidine which is about four and a half times the average amount contained in other globuline compared. The albumin (B) constitutes an interesting protein containing both P and S in the molecule. A determination of the biological value of these fractions is contemplated.

### 184. The mucilage of Fenugreek (*Trigonella Foenum Greacum*).

B. N. SASTRI and C. R. HARIHARA IYER, Bangalore.

The mucilage isolated from the seeds, has been found to be a mannogalactan containing the two sugars in equal quantities. As usually prepared, it is associated with a nitrogenous impurity containing phosphorus, which could be precipitated by saturating the aqueous solution with magnesium or ammonium sulphate. A purified preparation, free from phosphorus and nitrogen, has been obtained thus showing that the mucilage is only a mannogalactan and not a silicophosphoric ester of mannogalactan as indicated by previous work.

### 185. A new constant for oils and fats.

K. L. BOSE and M. GOSWAMI, Calcutta.

With oils and fats containing unsaturated linkages the hypochlorous acid gives only addition products and no substitution occurs as in the case of iodine value determination.



The determination of hypochlorous acid value affords another additional advantage in the fact that this involves the simultaneous determination of saponification value.

186. The linolic acid content of milk-fats. Part I.—The butter-fat of the cow.

P. RAMASWAMI AYYAR and J. D. VASAVADA, Bangalore.

A sample of cow's ghee made from the milk of a Bangalore cow had a saponification value of 229.8 and an iodine value of 43.4. Oxidation of 15 grams of the saponified fat yielded after purification about 0.9 gram of a tetrahydroxystearic acid melting at 148–150°C., corresponding to about 5 per cent. of linolic acid on the fat as such.

Similar work on buffalo's ghee and other milk-fats is in progress. The significance of linolic acid content in relation to the latest researches on fat metabolism in animal bodies is discussed.

187. The fat from the seeds of *Garcinia Gambogia*.

P. RAMASWAMI AYYAR and J. D. VASAVADA, Bangalore.

The seeds kindly supplied by the Chief Conservator of Forests, Travancore, consisted of 46.7 per cent. of kernels and 53.3 per cent. of shells.

The former yielded to petroleum ether 37.6 per cent. of a pinkish white fat which had the following analytical constants:—

Solidification point	=29.3°C.
Specific gravity	=0.8948.
Iodine value	=44.2.
Saponification value	=184.3.
Unsaponifiable matter	=1.2 per cent.

The detailed composition of its fatty acids is under investigation.

188. Investigation of the component fatty acids and glycerides of *Mowha* and *Garcinia Morella* (Tamal) fats.

D. R. DHINGRA and G. L. SETH, Lahore.

The component fatty acids and glycerides of the two fats have been determined fully and it has been found that they consist mainly of palmitic, stearic, and oleic acids, with small amounts of myristic and linoleic acids. They are good sources of stearine which can be profitably extracted on a commercial basis.

189. Studies of the component fatty acids and glycerides of some uncommon milk fats.

D. R. DHINGRA, Lahore.

The composition of the fatty acids and glycerides of goat's milk and sheep milk fats has been investigated fully and their relationship with the ordinary butter fats established.

190. Studies in fish oils—chemical analysis of the body oils of Rohita, Mirgal and Dhain fish (fresh-water fish from Bengal).

N. C. DATTA and B. N. BANERJEE, Bangalore.

A detailed examination of the different constituent and the composition of complex mixtures of fatty acids present in the fish oils has



been done. These body oils contain highly unsaturated acid of  $C_{18}$ ,  $C_{20}$ , and  $C_{24}$  series like the cod-liver oils.

Compared to the unsaturated acids in the liver oil of Rohita investigated by J. K. Choudhury and Pulin Behari Sarcar (*Journal, Indian Chemical Society*, 1930, Vol. VII, 309).

Liver Oil.			Body Oil.		
Solid acid	..	28.1%	Solid acid	..	28.7%
Liquid acid	..	71.9%	Liquid acid	..	71.3%
Mixed fatty acid I.V.		149.6	Mixed fatty acid I.V.		130.2
Mean mol. wt.	..	295.3	Mean mol. wt.	..	290.0
I.V. of liquid acid	..	180.9	I.V. of liquid acid	..	161.5

The body oil of Rohita was found to contain the same unsaturated acid as liver oils—the only difference being that the percentage of Hexadecatrienoic acid and Linolenic acid in the body oil is slightly lower. There is no Asellinic acid in the body oil: there is a small percentage of Linolic acid in the body oil which is absent from the liver oil.

### 191. Cashew shell oil. Part II.

Y. K. RAGHUNATHA RAO, Bangalore.

In continuation of communication (*Indian Science Congress*, 1931, *Section of Chemistry*), country-rendered shell oil from *Anacardium Occidentale* has been analysed. The oil has Sp. Gr.  $30(1.01)$ , acid value (64.2), saponification value (101.5), iodine value (328).

Acids (45–55 per cent.), chiefly anacardic acid ( $C_{22}H_{32}O_3$ ), have iodine value (331), give a violet colour with ferric chloride, give equivalent and molecular weight in benzene (340).

Phenols (35–45 per cent.) have iodine value (305), colour pink with ferric chloride and consist chiefly of cardol. Combustion of the purified liquid and molecular weight in benzene (308) support the formula  $C_{21}H_{30}O_2$ . It is being further studied.

### 192. Oil-soluble vitamin A in some pulses and fishes of Bengal.

H. N. BANERJEE and N. C. NAG, Calcutta.

In continuation of the work in connection with the chemical examination of some pulses and their oils (*Proceedings, Indian Science Congress*, XVI and XIX; *Trans. Bose Institute*, Vol. VI and Vol. VII) further progress has been made. Vitamin A has been detected by  $SbCl_3$  test in some of the oils extracted from the pulses, the vitamin being most pronounced in the unsaponifiable portion. It has been possible to take a few absorption band spectrographs of the  $SbCl_3$  blue compound. Oils from some fishes, such as Rohit, Catla, and Ilisha, have also been found to give positive reaction. Comparison has been made with Cod-liver Oil. The reaction given by oils from *Cicer arietinum* (chhola) and Ilisha is most pronounced. As regards keeping quality, oil from *Cicer arietinum* has been found to give the vitamin test for months, while Ilisha Oil has been found to give the reaction for two to three weeks. Keeping quality and methods of extraction are still under observation. Tinctometric tests are in progress.



## 193. Artificial lubricating oil from oleic acid.

J. K. CHOWDHURY and A. C. CHAKRAVARTY, Dacca.

A viscous oily product has been obtained by polymerisation of oleic acid at 100°C. in an inert atmosphere with stannic chloride as catalyst. Mechanical stirring has been found to favour the reaction. With the progress of polymerisation, density, refractive index, and viscosity increased while the iodine value decreased. The maximum viscosity obtained was 285.1 E1 at 26.5°C. and the minimum iodine value 19.48, the corresponding figures for oleic acid being 34.63 and 79 respectively.

The viscous product was decarboxylated by treatment with zinc dust at 360° for 2½ hours. The acid value fell from 178.6 to 12 by this treatment and hence the product was mainly a hydrocarbon in composition. The oil thus obtained, was highly viscous and was similar to unrefined petroleum lubricants in colour and smell, and, like petroleum products, exhibit fluorescence to a remarkable degree.

## 194. The effect of some electrolytes on the permeability of the intestinal membrane towards sugars.

K. C. SEN, Muktesar.

The object of this paper is to consider the mechanism of intestinal absorption of sugars from the point of view of colloid-chemical theories, and to find out how far the facts arrived at experimentally can be explained by such theories. It is shown that certain ions definitely affect the permeability of the gut wall, and the calcium ion has apparently a specific effect on both *in vitro* and *in vivo* experiments, a fact which is not easily explained by the ordinary physico-chemical theories. The results are discussed in relation to the colloidal properties of the intestinal membrane.

195. Investigation on the proteolytic enzymes and their activators in *Calotropis Gigantia* (Ákanda).

K. P. BASU and M. C. NATH, Dacca.

A proteolytic enzyme somewhat similar to papain has been found in the milky juice of Ákanda. It hydrolyses gelatine, egg-albumin, casein, and fibrin, the optimum pH being 5 which is also the pH of the milky juice itself and the optimum temperature, 50°C. The enzyme is activated by potassium cyanide, sulphuretted hydrogen, and cystein but not by cystin. Peptone is not attacked even in the presence of activators and hydrolysis of the complex proteins proceeds only to the stage of peptone. Pyrophosphate retards hydrolysis but not in the presence of sulphuretted hydrogen or cyanide. Activation is probably brought about by a sulphur compound in SH but not in S-S form. A white crystalline sulphudryl compound of melting point, 98°C., has been isolated from the juice and this is probably the activator.

Further work is in progress.

## 196. Utilisation of waste molasses. Part I.—The preparation of smoking tobacco.

M. Q. DOJA and M. HUSSAIN, Patna.

In view of the increasing importance of the sugar industry in India an attempt has been made to solve the problem of the utilisation of waste molasses, by using them in the preparation of smoking tobacco manufactured by crude indigenous methods. We have tried to investigate the preparation of smoking tobacco in a strictly scientific manner. The tobacco leaves have been powdered in a disintegrator and the mixing of



the powdered tobacco and molasses has been carried out in roller mills. Variations have been tried with regard to the relative proportion of molasses and tobacco and the temperature of mixing the two substances. The nicotine content of the tobacco leaves and the quality of the product obtained in each case have been investigated. The 'lasting power' of the finished product has been determined by means of a specially designed apparatus.

197. Utilisation of Avaram (*Cassia auriculata*) bark.

K. A. N. RAO and S. L. JANNIAH, Bangalore.

Extracts containing 40 per cent. tannin have been prepared from Avaram bark and large-scale tanning experiments are being conducted with it. The paper also contains numerous data with regard to the day-to-day variation of tannin and precipitate of the vat-liquors during the course of bark-tanning.

198. Treatment of wood with creosote-water emulsions.

C. VARADHAN and K. ASWATHNARAIN RAO, Bangalore.

Stable emulsions of wood tar and coal tar creosotes with water (1 : 1) have been successfully used for pressure treatment of timber, both in the laboratory and in semi-commercial plant. Absorption data for a number of woods have been obtained.

199. Nutritive value of hill pasture. Part I.—The mineral-content of some pastures in relation to rainfall and drought.

A. C. ROY and K. C. SEN, Muktesar.

In the course of some nutritional experiments, it was necessary to estimate the lime and phosphoric acid content of some local pastures ordinarily used for the feeding of cattle, and in some winter-cut hay, a surprisingly low amount of phosphoric acid was found. An elaborate experiment was therefore planned to study the effect of environment on the mineral content of pastures from three specially chosen fields, and in this paper an account is given of the monthly variation of some mineral constituents and a correlation is made between the rainfall or drought and availability of the minerals for the growing pastures. The importance of this seasonal variation from the point of view of animal nutrition is also discussed.

200. Studies in the nutritive value of Indian vegetable food-stuffs. Part V.—The nutritive value of *Eleusine coracana*.

S. P. NIYOGI, N. NARAYANA, and B. G. DESAI, Bombay.

*Eleusine coracana* (Ragi or Nagli) is a staple millet of the Mysore State and contains 6–9 per cent. of protein. Consecutive treatment of the flour with dilute salt solution, cold 70 per cent. alcohol and subsequent boiling remove 70 per cent. of the total nitrogen. The residual nitrogen cannot be extracted even by prolonged treatment with dilute alkali. The protein soluble in cold alcohol was isolated and analysed. The protein contained both sulphur and phosphorus and was characterised by a very low percentage of the basic amino-acids and a high tryptophane-content.

Feeding experiments on albino rats were conducted at a 5% level of protein intake. The average digestibility and biological value of the total proteins of this millet were found to be 77.5 and 90.5 per cent. respectively.



201. Action of *B. coli* on conjugated bile acids.

K. P. BASU and S. C. CHAKRAVARTY, Dacca.

The object was to investigate if in the bile cycle the intestinal bacteria bring about a cleavage of the CO-NH linkage of the conjugated bile acids. A physiological sodium chloride suspension of *B. coli*, which had been previously cultured three times in bile salt medium, was employed. The action was tried on glycocholic and taurocholic acids at 37°C., at different pH using phosphate buffers. Using Willstätter's method of estimation of amino-acids no cleavage could be detected either in acid, neutral or alkaline medium.

## 202. The electronic mechanism of elimination of radicals from sulphonium hydroxides.

C. K. INGOLD and K. I. KURIYAN.

Sulphonium hydroxides may decompose in two possible directions; one giving an olefine and the other an alcohol. It was found that the relative ease of elimination of radicals as olefines is a measure of the relative electron-affinity of radicals. The order of the ease of elimination of radicals is

ISO- $\dot{\text{P}}$ ROPYL > ETHYL > N-PROPYL > N-BUTYL > ISO-BUTYL.

## 203. Grouping of electrons and stability of sulphonium compounds.

C. K. INGOLD and K. I. KURIYAN.

There is evidence to show that a sextuple grouping of electrons confers stability to a compound. Jessop and Ingold (*J.C.S.*, 1930, 713) isolated Di-methylsulphonium 9 fluorenylide. It is very unstable. The present workers stabilised the 9 carbon atom by di-nitrating the fluorenyl group, i.e. prepared Di-methyl di-nitro sulphonium fluorenylide. The importance of the preparation lies in the fact that a compound containing a carbon atom with a 'lone pair' of electrons has been isolated.

## 204. Studies in the ligno-cellulose group. Part III.

P. K. DAS and H. K. SEN, Calcutta.

The question whether lignin is chemically combined with cellulose in ligno-cellulose has been attempted to be decided by noticing the degree of acetylation—

(1) of sawdust on treatment with acetic acid, acetic anhydride mixture under 5 atmosphere pressure and corresponding steam heat;

(2) of cellulose isolated from sawdust by Schmidt's chlorine-peroxide process;

(3) of cellulose separated from sawdust by Cross and Bevan's process.

In all cases when the lignin is removed, the maximum acetyl value corresponding to diacetyl is obtained. Even on examining the acetic acid value after a few hours of acetylation an increased acetic acid value is noticed both in the case of chlorine-peroxide cellulose and Cross and Bevan cellulose. This would lend support to the view formerly expressed by the authors that lignin is chemically combined with cellulose in ligno-cellulose, for the most part at any rate.

## 205. Adsorption of alkali by cotton and modified celluloses.

TARAPADA BHOWMIK and H. K. SEN, Calcutta.

Alkali adsorption figures at various concentrations of alkali have been found, from which no evidence can be established that a real chemical



or additive combination between the alkali and the cellulose takes place. In some cases, however, molecular or multimolecular proportions of alkali are adsorbed, but the variations of such ratios with different concentrations of alkalis are so great that no conclusion can be drawn, contrary to views put forward by a few workers in this line.

## 206. Explosion of oxy-hydrogen mixtures.

H. N. CHATTERJEE, A. N. MITRA, and H. K. SEN, Calcutta.

While measuring the explosion temperatures of oxy-hydrogen mixtures in the presence of heated platinum wires, it was found that the catalytic effect of the different specimens of wires used was great on the temperatures of ignition. In order to investigate into this catalytic influence more thoroughly, we exploded oxy-hydrogen mixtures enclosed in soap-bubbles over electrically heated platinum wires of different catalytic conditions. On exploding these mixtures over plain, roughened, and platinised platinum, it was found that the ignition points with roughened wires were lower than those with plain wires and the temperature of ignition over platinised platinum was the least. We obtained similar results by igniting the gas mixtures in glass bulbs in which platinum wires were stretched axially, the temperature being measured in this case by observing the change in the electrical resistance of the wires.

Experiments on the order of reaction between oxygen and hydrogen when they combine in a heterogeneous way in presence of a heated platinum wire are now in progress. They point primarily to a bimolecular nature of the reaction.

## 207. A high pressure electrolytic cell.

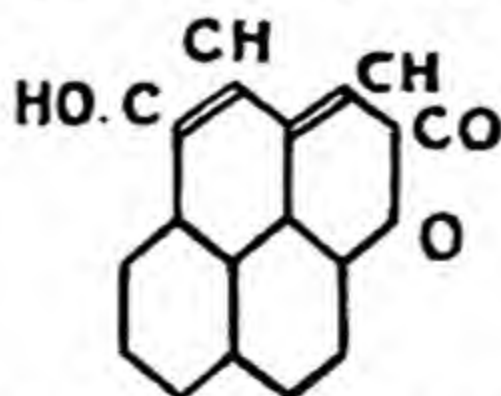
S. S. GHOSH and H. K. SEN, Calcutta.

The introduction of a *positive* compensator and of a liquid manometer in the circuit has decidedly improved the working facility of the cell already described in the Journal of the Institute of Chemical Engineers, London (1932). This *positive* compensator allows of the variation in volume of either the oxygen or the hydrogen compartment with such an exactness that the ratio 2 : 1 between the hydrogen and the oxygen compartments can be easily maintained. Data relating to power consumption have been experimentally determined. A parallel combination of three cells works at 1.55–1.63 volts. The electrical energy required for producing 1,000 c.ft. of hydrogen at 120 atmospheres is 112 K.W.H. Taking energy at  $\frac{1}{4}d.$  per K.W.H., the cost of electrical energy for producing 1,000 c.ft. of  $H_2$  and 500 c.ft. of  $O_2$  is 2 shillings and 4 pence. The gases are 99.9% pure.

## 208. Some peri-peri-naphthindenofuran derivatives.

B. B. DEY and (MISS) K. RADHABAI, Madras.

A closer investigation of the properties of 5-hydroxy-2-keto-peri-peri-naphthindenofuran (Dey, *J.C.S.*, 1915, 1631) of the following formula



has now been made. The melting point of the substance, purified by several crystallisations from pyridine, is found to be much higher ( $330^\circ$ ) than that previously reported ( $280^\circ$ ). The enolic hydroxyl is found to



be so markedly acidic that it dissolves even in cold sodium carbonate, and the molecule can be esterified like a carboxylic acid by alcohols in the usual manner. The methyl (m.p.  $236^{\circ}$ ), ethyl (m.p.  $226^{\circ}$ ), and propyl (m.p.  $196^{\circ}$ ) ethers have now been prepared by refluxing with the corresponding alcohol and sulphuric acid. These alkyl derivatives, however, are not to be regarded as esters, for they cannot be hydrolysed by boiling with 4N-caustic soda, while the corresponding acetyl derivative (m.p.  $215^{\circ}$ ) is readily de-acetylated under these conditions.

The 3-chloro- and 3-bromo-, 5-hydroxy-2-keto-peri-peri-naphthindenofurans have also been synthesised. On halogenating  $\beta$ -naphthapyrone-4, acetic acid under the usual conditions, the halogen seems to enter position 3 exclusively and not to attack the reactive methylene H-atoms. The 3-chloro-acid forms hard tetragonal prisms (m.p.  $154^{\circ}$ ) and decomposes above its melting temperature into 3-chloro-4-methyl- $\beta$ -naphthapyrone (m.p.  $136^{\circ}$ ), while the bromo acid forms soft needles (m.p.  $190^{\circ}$ ) and passes into 3-bromo-4-methyl- $\beta$ -naphthapyrone (m.p.  $149^{\circ}$ ). They are converted almost quantitatively into the 3-chloro- and the 3-bromo-naphthindenofurans which crystallise from pyridine in orange-yellow needles not melting up to  $350^{\circ}$ , and yield acetyl derivatives crystallising in orange prisms melting at  $230^{\circ}$  and  $214^{\circ}$  respectively. The alcoholic solutions of all these derivatives show an intense green fluorescence.

## 209. Cis- and Trans-acids from 4-methyl- $\beta$ -naphthapyrone.

B. B. DEY and A. K. LAKSHMINARAYANAN, Madras.

In addition to the cis-acid (m.p.  $146^{\circ}$ ) reported previously (Dey, *J.C.S.*, 1915, 1630), an acid (m.p.  $110^{\circ}$ ) which is apparently the trans-isomer has now been prepared by boiling the alkaline solution of the pyrone with mercuric oxide. The behaviour of the two acids on heating to their melting points—both pass into the pyrone with evolution of steam—and on crystallising from boiling solvents like alcohol, acetic acid etc., is so similar that the allocation of configurations on the usual grounds of stability is not possible here. Exposure of a dry chloroform solution of the two acids to ultra-violet rays for the same period has, however, revealed a difference: while the trans-acid (m.p.  $110^{\circ}$ ) is slowly changed into the pyrone (m.p.  $178^{\circ}$ ), the cis-acid (m.p.  $146^{\circ}$ ) seems not to be affected at all.

The 3-chloro- and the 3-bromo-4-methyl- $\beta$ -naphthapyrone also show a curious difference, though only of a quantitative character, when boiled with alkali. It had been reported (Dey, *loc. cit.*), that 3-chloro-4-methyl- $\beta$ -naphthapyrone was distinguished from all other 3-halogenated coumarins by not yielding the expected furan derivative, but instead, a remarkably stable chloro-coumarinic acid. The observation has now been made that although chloro-coumarinic acid is the sole product obtained under the conditions employed previously, prolonged treatment with boiling strong potash converts a portion into the hitherto unknown  $\beta$ -naphtha-furan-carboxylic acid (m.p.  $240^{\circ}$ ).

The 3-bromo-pyrone, on the other hand, rapidly changes on boiling with dilute aqueous alkali into the furan derivative only, no bromo-coumarinic acid being isolated in this case.

## 210. Coumarin-8-carboxylic acid.

B. B. DEY and Y. SANKARANARAYANAN, Madras.

This compound does not appear to have been described in literature. It has now been synthesised from 3-aldehydo-salicylic acid prepared from hexamine and salicylic acid by the method of Duff and Bills (*J.C.S.*, 1932, 1987) with a view to study the influence of the carboxyl-group in the ortho-position on the stability of the cis- or coumarinic acid. It crystallises from hot water in shining needles (m.p.  $242^{\circ}$ ).



211. Measurement of E.M.F. of the system :  $\text{H}_2(\text{Pt.}) \text{HCl. (c).}$   
 $\text{Hgcl. Hg.}$  with hydrochloric acid solution below 0.01 N.  
 concentration.

K. KUMAR, Calcutta.

In presence of dissolved oxygen in hydrochloric acid solution pure mercury reacts with hydrochloric acid forming calomel and solutions below 0.01 N. appreciable decrease of hydrochloric acid concentration is produced. An exact e.m.f. measurement, therefore, is not possible. When, however, dissolved oxygen is removed by saturating hydrochloric acid solution with pure nitrogen, no change in concentration of the acid solution takes place and reproducible e.m.f. measurements are possible even in very dilute solutions.

212. Condensation of ethylene chlorhydrin with p- and o-nitro-phenols.

MISS B. N. KATRAK, Bombay.

With a view to prepare compounds which might possess antipyretic properties, ethylene chlorhydrin has been condensed with p- and o-nitro-phenol in presence of dilute alcohol, the corresponding nitro-ethers being formed. P-acetyl-amino-phenol has also been similarly condensed. Several derivatives of these compounds have also been obtained.

213. The condensation of ethylene chlorhydrin with naphthols and a study of the products obtained.

B. M. KAPADIA, Bombay.

Naphthols have been condensed with chlorohydrins.

$\alpha$  and  $\beta$ -naphthols on condensation with ethylene chlorhydrin yield  $\beta$ -hydroxyethyl- $\alpha$ -naphthyl ether and  $\beta$ -hydroxyethyl- $\beta$ -naphthyl ether respectively. Acetyl and benzoyl derivatives have been prepared. Further work is in progress.

214. Condensation of ethylene chlorhydrin with resorcinol and derivatives of the products.

D. C. MOTWAIN and T. S. WHEELER, Bombay.

With a view to preparing substances of therapeutic value resorcinol, mono-methyl ether of resorcinol, resacetophenone, and ethyl resorcinol have been condensed with ethylene chlorhydrin. The method of condensing consists in dissolving the substance in 40% KOH and then refluxing the solution with the required quantity of ethylene chlorhydrin.

Resorcinol gives two products, the *mono* and the *di- $\beta$ -hydroxy ethyl* ethers, of which the former has been prepared for the first time. The *diacetyl* derivative and the *dibenzoyl* derivative have also been prepared. The *monochloro* derivative  $\text{HO. CH}_2\text{. CH}_2\text{O. C}_6\text{H}_4\text{ Cl}$  gives no coloration with  $\text{FeCl}_3$ . The *dichloro* derivative is a liquid and hydrolyses slowly to the stable mono-derivative.

The *di- $\beta$ -hydroxy ethyl* ether of resorcinol has m.p.  $95-96^\circ\text{C}$ . Rind-fusz and others (*J.A.C.S.*, 1920, 42, 157) obtained m.p.  $81^\circ\text{C}$ , because they did not separate it from the mono ether. The *diacetyl*, *dibenzoyl*, and *dichloro* derivative have been obtained.

Resacetophenone and ethylene chlorhydrin give a *mono ether* in which the OH group in o-position to the  $\text{COCH}_3$  group cannot be replaced. The ether and its *mono acetyl* as well as *mono benzoyl* derivatives give violet coloration with  $\text{FeCl}_3$ . Its *phenylhydrazone* and *oxime* have been obtained. The p- $\beta$ -hydroxy ethyl ether of o-hydroxy-acetophenone con-



denses, in alcoholic solutions, with benzaldehyde in presence of KOH to give the corresponding *chalkone*. The reactions of this *chalkone* will be used to confirm the position of the free nuclear hydroxyl group by the synthesis of the corresponding flavone.

M-methoxy phenol and ethylene chlorhydrin yield the corresponding *hydroxy ether*.

Ethyl resorcinol, prepared from Resacetophenone, with ethylene chlorhydrin yields (1) the *hydroxy ethyl ether*. With  $\text{FeCl}_3$  it gives a violet coloration in alcoholic solution.

Further work is in progress.

## 215. Studies in the halogenation of toluene and its derivatives.

E. PAIS and T. S. WHEELER, Bombay.

I. (a) At present benzo tri-chloride, benzal bromide, and benzyl iodide represent the maximum substitution capacity for halogen (Cl, Br, I) of the toluene side-chain. The subject has now been studied in detail and the following new compounds have been obtained:—(1) *benzal chloro bromide*; (2) *benzo di-chloro bromide*; (3) *benzo chloro di-bromide*. It has been found that molecular bromine can displace chlorine from the side-chain under suitable conditions.

In this connection the exhaustive bromination of toluene in absence of a carrier has been examined and the following have been isolated for the first time:—(4) benzal bromide; (5) stilbene; (6)  $\alpha$  and  $\beta$  di-bromostilbene; and (7) *di-phenyl tetra-bromo ethane*.

To isolate these compounds which can be distilled only under very low pressures and which boil close together a technique for control of fractions by density determination has been evolved.

(b) The compounds numbered 1, 2, 3, 4, as well as benzo tri-chloride and benzyl iodide have been brominated in presence of a catalyst and the following substituted derivatives have been obtained. These have been orientated by conversion to the corresponding bromo-benzoic acid; from benzal chloro bromide *o*, *p*, *bromo benzal chloro bromide*, and *o-p*, *di-bromo benzal chloro bromide*; from benzal bromide *o*, *m*, *p* *bromo benzal bromide*; from benzo di-chloro bromide, *m* *bromo benzo-di-chloro bromide*, *m-p* *di-bromo benzo di-chloro bromide*, and *m-p-m*, *tri-bromo benzo di-chloro bromide*; from benzo-chloro di-bromide—*m-bromo benzo chloro di-bromide*, *m-p* *di-bromo benzo chloro di-bromide*, and *m-p-m* *tri-bromo benzo chloro di-bromide*; from benzo-trichloride—*m* *bromo benzo tri-chloride*, *o-m*, and *m-p*, *di-bromo benzo tri-chloride* and *m-p-m* *tri-bromo-benzo tri-chloride*; from benzyl iodide *p-bromo benzyl iodide*, *o-p* *di-bromo benzyl iodide*, and *o-p-o* *tri-bromo benzyl iodide*.

(c) Benzyl bromide and benzal bromide have been chlorinated in the absence of a catalyser, both in the dark and in the light. It is found that light plays an active part in the chlorination of these compounds at various temperatures. The following have been obtained on chlorination in the dark:—from benzyl bromide, benzo trichloride, *benzal chloro bromide*, *m-chloro benzo di-chloro bromide*, *m-p*, *di-chloro benzo di-chloro bromide*, and symmetrical *di-p-chloro phenyl di-chloro di-bromo ethane*; from benzal bromide, benzo-tri-chloride, *benzal chloro bromide*, *p-chloro benzal chloro bromide*, *m-p* *di-chloro benzo di-chloro bromide*, and *o-p*, *di-chloro benzal chloro bromide*.

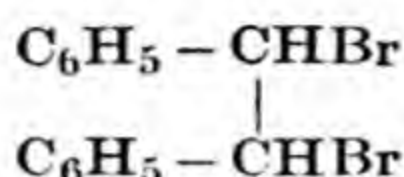
Benzyl bromide and benzal bromide chlorinated in the light at 30°C. and 110°C. yielded only benzo tri-chloride.

(d) Experiments have been made on the action of potassium iodide and sodium iodide on benzal chloride, benzo tri-chloride and benzal bromide, with and without solvent. The reaction is vigorous in the former case and iodine vapours are evolved.

Compound containing an atom of iodine and any other halogen



in the side-chain are quite unstable. Benzal chloride and potassium iodide gives tarry matter and stilbene; while benzal bromide and potassium iodide yields  $\alpha$  di-bromo stilbene



Benzal bromide is highly reactive. Thus with pyridine in presence of copper powder it gives presumably *phenyl di-pyridyl methane*. This type of condensation with pyridine appears to be new.

II. Molecular weight determinations of the compounds by a modification of the camphor method have been made.

III. The density of the new liquid halogen compounds has been accurately determined to fix the molecular volume of halogen in the side-chain of aromatic compounds.

## 216. A study of the production of camphor.

B. G. S. ACHARYA and T. S. WHEELER, Bombay.

The production of camphor from pinene is being systematically studied, with a view to improving the yield and to replacing expensive by cheap chemicals. The work on the first step, the production of pinene hydrochloride from pinene is now complete. It has been found possible by introducing improvements to raise the yield to 76%, the usual figure published being less than 60%. It has not been found possible to substantiate the claims made in patents for quantitative yields of camphene from pinene hydrochloride. The best yield we have obtained is 83%. It is hoped that the results of this work will provide a reliable guide to the value of the many published patents on the synthetic production of camphor from pinene and will indicate the best method for working on an industrial scale.

## 217. Condensation of methyl-o-toluidine and ethyl-o-toluidine with chloral hydrate.

A. N. MELDRUM and A. H. ADVANI, Bombay.

Methyl-o-toluidine and ethyl-o-toluidine were condensed with chloral hydrate to *p-( $\alpha$ -hydroxy- $\beta$ -trichloro ethyl)-o-methyl toluidine* and *p-( $\alpha$ -hydroxy- $\beta$ -trichloro ethyl)-o-ethyl toluidine*. These condensation products were converted into *nitrosoamines* by the action of nitrous acid. *Acetyl* derivatives were also prepared. The *mono* and *diacetyl* derivatives of the former yielded *p-( $\beta$ -dichloro-ethylene)-o-methyl aceto-toluidide* on reduction with zinc dust and acetic acid.

*Para-N-methyl-acetyl amino-m-toluic acid* was also prepared from the diacetyl derivative; this on hydrolysis yielded *p-N-methyl-amino-m-toluic acid* which has been synthesised by J. Houben (Ber. 1909, 42, 4490).

## 218. Kinetics of heterogeneous organic reactions. The reactions between organic halogen compounds and solid inorganic salts.

K. E. LALKAKA and T. S. WHEELER, Bombay.

The kinetics of the reaction between benzyl chloride and solid silver nitrate in presence of inert solvents is being studied.

A preliminary qualitative study has been made of the action of solid nitrates on benzal chloride and bromide. Benzylidene nitrate is unstable and at once breaks down forming benzoic acid, a hydrogen atom



migrating from carbon to oxygen. Benzotrichloride and solid silver nitrate in the absence of water or other solvent give benzoic acid and a resinous substance. The hydrogen necessary for the formation of the acid appears to be derived in the production of the resin. Similarly dry triphenylchloromethane and solid silver nitrate give triphenylcarbinol and a resin.

219. The kinetics of heterogeneous organic reactions. A study of the benzoin reaction.

D. R. NADKARNI and T. S. WHEELER, Bombay.

Existing literature does not make it clear whether potassium cyanide and benzaldehyde in the absence of all solvents will yield benzoin. The discordant published results have now been traced to the fact that if pure benzaldehyde and pure potassium cyanide be employed, then benzoin in 99.6% yield can be obtained by shaking these reagents at room temperature for some days. The reaction is completely inhibited if less pure potassium cyanide be used. This inhibiting effect appears to be associated with the presence of calcium.

The kinetics of the heterogeneous reaction between potassium cyanide and benzaldehyde in the absence of all solvents has been studied at 100° and at 30°. The reaction is autocatalytic and is represented by

Rate of formation of benzoin

$$=k_1[\text{C}_6\text{H}_5\text{CHO}]^2 [\text{Benzoin}] + [\text{KCN}][\text{C}_6\text{H}_5\text{CHO}]^2$$

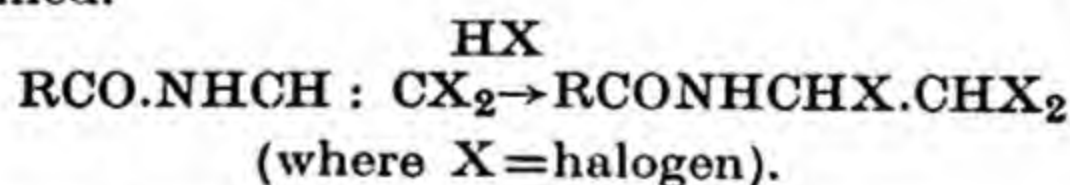
The main reaction is independent of the amount of KCN present. Addition of small quantities of water alters completely the kinetics of the reaction, which then becomes of zero order.

A new method has been worked out for estimating the quantity of benzoin formed in an experiment.

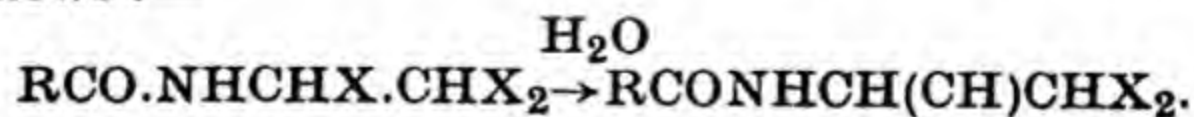
220. Study of the constitution of the reduction products of chloral and bromal amides.

B. H. YELBURGI and T. S. WHEELER, Bombay.

By the action of dry hydrogen chloride and also of hydrogen bromide on the reduction product of chloral and bromal amides addition compounds are obtained.



The compounds are unstable and on exposure gives a hydroxy compound as follows:—



That the compound obtained on hydrolysis is an hydroxy compound is shown by studying a number of derivatives.

All the evidence collected shows that the reduction products of chloral amide ( $\text{RCO.NHCH}(\text{OH})\text{CCl}_3$ ) are  $\text{RCONHCH} : \text{CX}_2$  and not  $\text{RCONHCH}_2\text{CHX}_2$  as hitherto supposed.

221. The gaseous equation of state.

T. S. WHEELER, Bombay.

In a recent paper (*Phil. Mag.*, 1932, 604) the author has shown theoretically that the second virial coefficient (B) of a gas of which the



molecules repel and attract one another by forces respectively  $\frac{\lambda}{r^n}$  and  $\frac{\mu}{r^m}$  can be expressed by an equation of the form

$$B = C_1 \left( \frac{\lambda}{T} \right)^{\frac{3}{n-1}} + C_2 \left( \frac{\mu}{\pi} \right)^{\frac{3}{m-1}}$$

This equation has now been applied to calculate the second virial coefficients of helium, neon, argon, hydrogen and nitrogen with satisfactory results. The relation of this expression to the more complicated expression of Lennard-Jones

$$B = K \left[ \left( \frac{\lambda}{T} \right) \left( \frac{T}{\mu} \right) \right]^{\frac{3}{n-m}} F \left[ \left( \frac{\mu}{T} \right) \left( \frac{T}{\lambda} \right)^{\frac{m-1}{n-1}} \right]$$

is being examined.

222. Action of nitric acid on (1) p-( $\alpha$ -hydroxy- $\beta$ -trichloro ethyl)-o-methyl toluidine; (2) p-( $\alpha$ -hydroxy- $\beta$ -trichloro ethyl)-o-ethyl toluidine; (3) p-( $\alpha$ -hydroxy- $\beta$ -trichloro ethyl)-dimethyl aniline and the action of bromine on the first two compounds.

A. H. ADVANI and T. S. WHEELER, Bombay.

The first two condensation products on treatment with strong nitric acid in the cold yielded the *mononitro compounds*. When the reaction was allowed to proceed in warm nitric acid, in both the instances, *nitro-nitramino* were obtained. The mononitro compounds yielded *diacetyl derivatives* whereas the dinitro compounds yielded *monoacetyl derivatives*.

The dinitro compound from the first condensation product, on exhaustive nitration yielded a known substance:--4:6-trinitro-methyl toluidine melting at 119° (Annalen 1905, 339, 221) which on treatment with strong sulphuric acid gave a *nitrosoamine*. The dinitro compound also yielded a *nitro-nitramino carboxylic acid*.

Para-( $\alpha$ -hydroxy- $\beta$ -trichloro ethyl) dimethyl-aniline on nitration in the cold yielded the corresponding di-nitro compound and in warm nitric acid gave a *nitro-nitramino chloral compound*. The condensation product on exhaustive nitration gave a known substance 2:4:6 trinitro-N-methyl-nitraniline (R., 1883, 2, 108, 305). The first two products of nitration gave each a *monoacetyl derivative*.

The first two condensation products on bromination yielded *monobromo compounds* whilst each of these compounds gave a *diacetyl derivative*. The diacetyl derivative of the former on oxidation was converted into a *bromo-monobasic acid* melting at 201°.

Further work is in progress on the bromination of all the three condensation products and the action of phosphorus pentachloride on the nitration products mentioned above.

223. Effect of temperature on the formation of salicylic acid derivatives.

N. W. HIRVE, Bombay.

On sulphonating salicylic acid, 5-nitro-salicylic acid alone was obtained by (a) Mendius (A., 1857, 103, 45), by (b) Remsen (A., 1875, 179, 137); by (c) Hirsch (Ber., 1900, 33, 3239); and by (d) Meldrum and Shah (Soc., 1923, 1986).



As heat is developed on addition of sulphuric acid to salicylic acid, the sulphonation was always carried out at high temperature and some even heated the mixture to 100° and above.

Having obtained 3-sulpho-salicylic acid indirectly from 5-nitro-3-sulpho-salicylic acid, and having found a great difference in the solubility in water of the acid potassium salts of 3-sulpho- and 5-sulpho-salicylic acids, the method was successfully applied to the isolation of 3-sulpho-salicylic acid from the reaction mixture in small quantities.

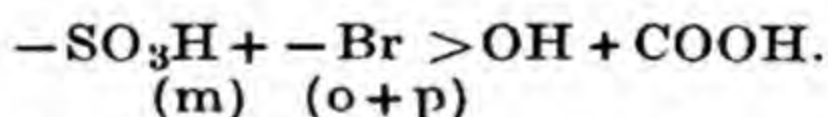
Low temperature favours the formation of 3-sulpho-salicylic acid; but the time required for the reaction to be complete is long. At high temperatures the reaction is finished quicker, but the main product is 5-sulpho-salicylic acid. The actual yields have been studied at various temperatures.

## 224. Stability of sulphonic acid group in the 4-sulpho-salicylic acid.

N. W. HIRVE and M. R. JAMBHEKAR, Bombay.

4-sulpho-salicylic acid has been nitrated and brominated and it has been shown that not only mono-nitro-sulpho and mono-bromo-sulpho-salicylic acids are obtained but also a dinitro-sulpho and a dibromo-sulpho-salicylic acid. This shows the unusual stability of the sulphonic acid group in position *four*, since the sulphonic acid group in 3-sulpho- as well as in 5-sulpho-salicylic acids is very easily eliminated either on bromination or nitration to give a 3 : 5 dibromo or 3 : 5 dinitro-salicylic acid.

Even on further action of bromine on 4-sulpho-salicylic acid a tri-bromo-sulpho-salicylic acid is obtained. This shows that the directing influence of

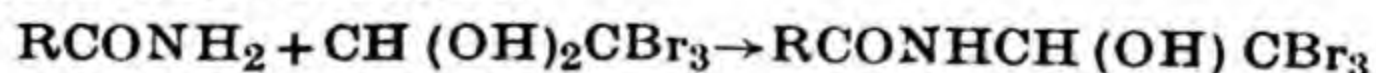


The various nitro-sulpho-, amino-sulpho- and bromo-sulpho-salicylic acids and their derivatives are described.

## 225. Condensation of bromal with aliphatic amides.

B. H. YELBURGI, Bombay.

Bromal hydrate was condensed with the aliphatic amides—from formamide to pelargonamide. The condensation took place as follows and bromal amides were obtained.



The condensation products were further reduced with zinc and acetic acid. In cases where the condensation products could not be directly reduced, their acetyl derivatives were reduced.

Various derivatives like acetyl and benzoyl were prepared.

## 226. Condensation of ethyl propyl acetoacetate with aromatic amines. Part II.

G. V. JADHAV, Bombay.

It has been shown in Part I (*J. Ind. Chem. Soc.*, 1931, 8, 681), that simple aromatic amines give simple anilides as well as carbamide derivatives according to the conditions of the reaction. The work is being extended to determine the effect of the substitution of a hydrogen atom of the amine by more negative groups like  $-\text{NO}_2$  or  $\text{Cl}$ . *o*-, *m*-, *p*-chloranilines and *p*- and *m*-nitranilines have been used. It has been found that



in all cases a simple anilide as well as a carbamide derivative are obtained according to the conditions of the reaction.

The constitution of the carbamide derivatives has been confirmed by their preparation according to Guha and Mistry (*J. Ind. Chem. Soc.*, 1930, 7, 793), as well as by converting them into simple acetchlor- or acetnitro-anilides by boiling them with acetic anhydride and fused sodium acetate.

## 227. Bromination of aromatic acid derivatives.

G. V. JADHAV and Y. I. RANGWALLA, Bombay.

It has been known that simple aromatic acids cannot be easily brominated and most of their bromo derivatives are obtained indirectly. M-bromobenzoic acid is obtained by direct bromination after heating benzoic acid and bromine in presence of water in a sealed tube for several hours. (Hübner, Ohly, and Phillip. *Annalen*, 1867, 143, 233; Hübner and Peterman. *Annalen*, 1894, 281, 2461.)

The work was undertaken to examine the distribution of bromine in esters containing two phenyl groups substituted in different ways.

The p-nitrophenyl benzoate resisted the action of bromine alone or in the presence of a solvent as well as usual catalysts like iodine, zinc chloride or anhydrous aluminium chloride. The method of Varma and Kulkarni (*J. Ind. Chem. Soc.*, 1926, 3, 291) was therefore applied and bromination was tried in the presence of nitric acid as well as fuming nitric acid, when in the latter case a nitro derivative in addition to the bromo compound was obtained. The bromo compound is p-nitrophenyl-m-bromobenzoate. The isolation of the bromo compound is difficult due to practically the same solubility as that of the original ester in the same solvent. Similarly the o-nitro-phenyl-benzoate gives two products. The work is being extended.

## 228. Condensation of phenols with acetone-dicarboxylic ester in presence of phosphorus pentoxide.

D. CHAKRAVARTI, Calcutta.

In continuation of the work in this line by the author (*J. Ind. Chem. Soc.*, 1931, 8, 129, 407, 619; 1932, 9, 25, 31, 389), it has been found that poly-hydroxy-phenols, e.g. resorcinol, orcinol, pyrogallol, etc. condense with acetone-dicarboxylic ester in presence of phosphorus pentoxide to form not chromones (as would be expected from Simonis' reaction) but coumarins, identical with the compounds, prepared by Dey (*J. Ind. Chem. Soc.*, 1915, 107, 1606) in presence of sulphuric acid. The condensation of the mono-hydric phenols, e.g. cresols, nitro-phenols and chloro-phenols, with acetone-dicarboxylic ester in presence of phosphorus pentoxide, is attended with difficulties, but interesting results are expected.

## 229. Friedel Crafts reaction with methoxy-coumarins and acid chlorides.

D. CHAKRAVARTI, Calcutta.

Methoxy-coumarins, e.g. 7-methoxy-4-methyl-coumarin, have been found to condense with acyl-chlorides in presence of aluminium chloride to form ketones. Attempts are being made to synthesise Coumaro- $\gamma$ -pyrones, where one  $\alpha$ -pyrone and one  $\gamma$ -pyrone ring are attached to the same benzene nucleus (Cf. Sen and Chakravarti, *Proc. Ind. Sc. Congress*, 1931, p. 158), from these ortho-hydroxy-coumaryl-ketones.



## 230. Observations on the chemistry of the B-Vitamins.

B. C. GUHA and P. N. CHAKRAVARTY, Calcutta.

Certain researches carried out lately on Vitamin B<sub>1</sub> indicate that it is probably a purine derivative. Progress has been made in the concentration of Vitamin B<sub>2</sub>, starting from Ox kidney or Ox liver. The process involves adsorption of the B<sub>2</sub> factor by charcoal and its subsequent elution by HCl. The chemical behaviour of vitamin B<sub>2</sub> suggests that it is a simple molecule, having neither pronouncedly acidic nor basic properties. The investigation is being continued.

## 231. Action of (a) Potassium chlorate and (b) Potassium bromate on Iodine.

M. S. SHAH and S. S. DESAI, Ahmedabad.

The reactions between (a) potassium chlorate and iodine, and (b) potassium bromate and iodine have been studied quantitatively with varying amounts of the reactants in absence and presence of traces of different acids such as sulphuric acid, nitric acid, hydrochloric acid, and acetic acid.

The reaction (a) proceeds in accordance with Bassett's equation :  $6\text{I}_2 + 10\text{KClO}_3 + 6\text{H}_2\text{O} = 6\text{KH}(\text{IO}_3)_2 + 4\text{KCl} + 6\text{HCl}$  (*J.C.S.*, 1890, 57, 761), only in presence of an acid and is totally inhibited when the acid is absent. The reaction (b), on the other hand, proceeds whether an acid is present or absent according to  $\text{I}_2 + 2\text{KBrO}_3 = 2\text{KIO}_3 + \text{Br}_2$ .

The authors have also studied the action of hydrochloric acid, hydrobromic acid and hydriodic acid at different dilutions on potassium chlorate, potassium bromate, and potassium iodate. The results obtained throw light on the mechanism involved in the above-mentioned reactions.

## 232. Applications of the methylsulphone method in proving the constitutions of substituted benzene sulphonic acids.

M. S. SHAH, C. T. BHATT, and D. D. KANGA, Ahmedabad.

The authors have shown previously (*Ind. Science Cong.*, 1931, p. 152) that methoxytoluene-sulphonic acids and sulphomethoxy-benzoic acids give *via* sulphonylchlorides, thiols and methylthiols, identical methoxybenzoic acid methylsulphones possessing definite crystalline forms and sharp melting points. With the help of the latter numerous substituted benzene sulphonic acids could be identified. The formation of methylsulphone constitutes a general method, alternative to that of sulphonamide, in determining the constitutions of sulphonic acids. Two applications of the method are given below :—

1. The nitrosulpho-benzoic acid obtained on sulphonation of benzoic acid followed by nitration (Limpricht and Uslar., *Annalen*, 1858, 106, 27; Taverne, *Rec. Trav. Chim.*, 1906, 25, 50) is 5-sulpho-3-nitrobenzoic acid since it produces through 5-sulpho-3-hydroxy-benzoic acid, 5-sulphonamido-3-methoxy-benzoic acid, m.p. 214°, and 3-methoxybenzoic acid 5-methyl-sulphone, m.p. 195°.

2. The product obtained on sulphonating m-toluidine is m-toluidine-6-sulphonic acid and not m-toluidine-2-sulphonic acid as described by Limpricht (*Ber.*, 1874, 7, 448) and Lorenz (*Annalen*, 172, 177) since the amino-sulphonic acids yields *via* 3-methoxytoluene-6-sulphonic acid, 5-methoxy-o-benzoic-sulphinimide, m.p. 242°, and 3-methoxy-benzoic acid 6-methyl-sulphone, m.p. 180°.



**233.** Condensation of chloral with 2-hydroxy-p-toluic acid and its methyl ether.

B. M. KAPADIA and A. N. MELDRUM, Bombay.

The authors have obtained the chloral derivatives of 2-hydroxy-p-toluic acid and its methyl-ether.

The main reactions are : (A) Condensation of chloral with (1)  $\text{C}_6\text{H}_3\text{CH}_3\text{OH} \cdot \text{COOH}$  and (2)  $\text{C}_6\text{H}_3\text{CH}_3\text{OCH}_3\text{COOH}$ ; so as to get (3)  $\text{C}_6\text{H}_2\text{CH}_3\text{OH}(\text{CHCCl}_3)\text{CO}$ , and (4)  $\text{C}_6\text{H}_2\text{CH}_3\text{OCH}_3\text{CO}(\text{CHCCl}_3)$ . (B) Reduction

of condensation product with zinc and acetic acid so as to get (5)  $\text{C}_6\text{H}_2\text{CH}_3\text{OH} \cdot (\text{CH}_2\text{CHCl}_2)\text{COOH}$  and (6)  $\text{C}_6\text{H}_2\text{CH}_3\text{OCH}_3\text{COOH}(\text{CH}_2 \cdot \text{CHCl}_2)$ . (C) Simultaneous hydrolysis and oxidation of the reduction product with sulphuric acid (conc.); the reaction converted compound (5) into (7)

$\text{C}_6\text{H}_2\text{CH}_3\text{OH}(\text{CH}_2\text{COOH}) \cdot \text{COOH}$  and compound (6) into (8)  $\text{C}_6\text{H}_2\text{CH}_3\text{OH} \cdot \text{COOH}(\text{CH}_2\text{COOH})$  (note that  $\text{OCH}_3$  group is simultaneously hydrolysed and compound (7) and (8) are different which is further proved by the m.p. of their mixture which is  $200^\circ$  and also as follows :—

Compound (7) was further condensed with chloral when (9)  $\text{C}_6\text{H}_3\text{CH}_3\text{OH} \cdot (\text{CH}_2\text{COOH})\text{CO} \cdot \text{CHCCl}_3$  was obtained while compound (8) gave

quite remarkably (10)  $\text{C}_6\text{H}_2\text{CH}_3\text{OHCOOH} \cdot \text{CH}_3$ . Compound (9) was reduced to get (11)  $\text{C}_6\text{H}_3\text{CH}_3\text{OH}(\text{CH}_2\text{COOH})\text{COOH}(\text{CH}_2\text{CHCl}_2)$

m.p.  $202^\circ\text{--}205^\circ$   $\xrightarrow[\text{and oxidation with H}_2\text{SO}_4]{\text{Hydrolysis}}$   $\text{C}_6\text{H}_3 \cdot \text{CH}_3 \cdot \text{OH}(\text{CH}_2\text{COOH})$ .

$\text{COOH}(\text{CH}_2\text{COOH})$  m.p.  $220^\circ$ .

The action of sodium hydroxide solution on compound (3) gave (13)

$\text{C}_6\text{H}_2\text{CH}_3\text{OH} [\text{CH}(\text{OH})\text{COOH}] \text{COOH}$  m.p.  $115^\circ$  and on (9) gave (14)

$\text{C}_6\text{H}_3 \cdot \text{CH}_3\text{OH}(\text{CH}_2\text{COOH})\text{COOH}[\text{CHOHCOOH}]$  m.p.  $246^\circ$  but the methyl ether compound (4) gave (15)  $\text{C}_6\text{H}_2\text{CH}_3\text{OCH}_3 \cdot \text{COCHCOOH}$ .

Acetaldehyde derivatives were produced by the action of alkali on the reduction compounds (5) and (6). The result is unconfirmed.

It should be noted here that the  $-\text{OH}$  group directs the condensation in ortho-position while the  $-\text{OCH}_3$  group directs it in the para-position alone.

**234.** A new synthesis of thio-ethers of hydroxy aromatic acids.

N. W. HIRVE, G. V. JADHAV, and Y. M. CHAKRADEO, Bombay.

Thionyl chloride acts on phenol and resorcinol, producing sulphides and sulphoxides. The reaction is vigorous even in the cold. With salicylic acid (o-hydroxy benzoic acid) the reaction of thionyl chloride produces all types of different anhydro compounds, possibly by the condensation of  $-\text{OH}$  and  $-\text{COOH}$  groups. The  $-\text{COOH}$  group was protected by converting it into its methyl ester  $-\text{COOCH}_3$ , and thus the methyl salicylate was treated with thionyl chloride alone. In the cold



there is no reaction, while on boiling for a long time, a high boiling liquid is obtained.

The reaction was also tried in the presence of finely divided copper which was converted into copper chloride and a di-methylsalicylate-thio-ether was obtained.

By bromination di-3-bromo-methylsalicylate-thio-ether is obtained, which gives 3-bromo-5-nitro-methylsalicylate by the action of nitric acid.

Similar condensations have been tried with the methyl esters of m-cresotinic acid, o-cresotinic acid, and 4-methoxy salicylic acid. Various derivatives of these condensation products also have been obtained.

### 235. Hydrogenation of common Indian oils.

M. S. PATEL and B. S. KANVINDE, Bombay.

The present investigation was undertaken to work out suitable data for the manufacture of tallow substitute by studying the hydrogenation of common Indian oils treated alone or in mixture in various proportions.

The rate of hydrogenation of groundnut oil is accelerated with the increase in the catalytic concentration. It is also found that at later stages the rate is almost proportional to the concentration of the catalyst.

In the case of supported catalyst, the temperature of reduction has considerable influence on the activity of the catalyst. A catalyst with 28.57% nickel on support when reduced at 500°C. is very active. The same catalyst when reduced at 320°C. is much less active. In spite of the larger area of the surface, its activity is found to be less than that of the corresponding unsupported nickel.

A supported catalyst containing about 28% nickel on support was found to be more active than that with 16% nickel.

In the hydrogenation of groundnut oil with low catalytic concentration the selectivity is exhibited more prominently than with higher catalytic concentration or with catalysts of high activity.

The melting point of groundnut oil at any particular degree of hydrogenation is the same irrespective of the nature and the concentration of the catalyst used during the hydrogenation.

The mixtures of oil consisting of glycerides of similar nature have in general a mean course of behaviour during hydrogenation with relation to the pure individual oils.

### 236. Starch and oil from Jowar (*Sorghum Vulgaris*).

M. S. PATEL and K. P. SHAH, Bombay.

The object of the work was to find out a suitable process for the extraction of starch from Jowar, to determine the exact conditions for obtaining maximum yields, and to study the nature of the bye-products.

The work has been completed and the results can be summarised as follows:—

1. Out of all the processes for the manufacture of starch from cereals the sulphurous acid process is found to be the most suitable for producing starch from Jowar. By this method the yields obtained are very high (about 52%) and the quality of the starch is good.

2. The traces of gluten in the final product (starch) could be removed by a weak solution of ammonia.

3. The slightly dull tinge of the starch obtained could be removed by bleaching. Passing chlorine gas into a thick suspension of starch in water is found to work better than solutions of sodium hypochlorite and bleaching powder.

4. It is difficult to separate the germs completely from the grain by flotation. It will be necessary to work some other process for this purpose.



5. The gelatinisation temperature of Jowar starch is  $67^{\circ}\text{C}$ .
6. Jowar starch granules are polygonal in shape and larger in size than those of the maize and rice starch.
7. The Jowar starch gave a good paste without any grit and acted as a good binding material for the size. The starch gets desized very easily.
8. The viscosity measurements showed that Jowar starch resembled wheat in its paste forming qualities.
9. The waste bran obtained after separation of starch from Jowar about 11% protein matter which compares favourably with the other cattle feeds.
10. The oil obtained from the germs of the Jowar grain is semi-drying oil resembling maize oil in its properties. Like the maize oil Jowar oil can be put to a number of uses : It has the following characteristics :—

Colour	..	..	..	Golden yellow
Solidifying point	..	..	..	$-8^{\circ}$ to $-9^{\circ}\text{C}$ .
Specific gravity	..	..	..	0.910 at $28^{\circ}\text{C}$ .
Refractive Index	..	..	..	1.467 at $28^{\circ}\text{C}$ .
Sap. Value	..	..	..	173.2
Iodine Value	..	..	..	126.8
Unsaponifiable matter	..	..	..	7.9%
Iodine value of the mixed fatty acids	..	..	..	130
Neutralisation value of the mixed fatty acids	..	..	..	166.5
Saponification value of the mixed fatty acids	..	..	..	186.1

### 237. Preparation of thorium nitrate and cerium nitrate from Indian monozite sand.

M. S. PATEL and S. G. DEV, Bombay.

The manufacture of Thorium nitrate and allied salts is a closely guarded secret. Recently demand for Thorium and Cerium nitrates has been created in this Presidency due to the development of gas mantle industry. There is however an international organization of gas mantle manufacturers which does not allow the sale of chemicals used in mantle industry to parties outside their pool, and so it is almost impossible for Indian gas mantle manufacturers to get their supplies of Thorium and Cerium nitrates. This work has been therefore undertaken to find out an economic process for the manufacture of these salts, from Indian Monozite sand. Samples of the sand have been analysed and have been found to contain 4 to 9.5% Thorium oxide.

### 238. Extraction of saponin from (1) soap-nuts (*Sapindus Trifoliatus*), (2) soap-pods (*Acacia Concina*).

M. S. PATEL and M. C. LAIWALA, Bombay.

To find out a suitable method for the economic extraction of saponins, which are used in large quantity in textile and beverage industry.

The pericarp of soap-nuts was found to constitute about 58% of the entire nut and the seed the rest. The pericarp on exhaustion with re-distilled methylated spirit yielded an extract which was treated with lead acetate and the lead salt of saponin decomposed with  $\text{H}_2\text{S}$ . The crude saponin thus obtained has been purified. The yield of saponin was found to be 6.8% of the pericarp. Further work is in progress.



239. Extraction and purification of strychnine and brucine from *Nux Vomica*.

M. S. PATEL and G. B. RAU, Bombay.

The *Nux Vomica* seeds which are found in abundance in India are exported in large quantities to foreign countries where they are used in the manufacture of Strychnine. This investigation has been undertaken to find out a cheap method suitable to Indian conditions by which the alkaloids can be manufactured from *Nux Vomica* seeds in this Presidency. The seeds have been extracted (1) with lime and methylated spirit, (2) with 40% redistilled methylated spirit.

It was found that the yield of alkaloids increased with the increase in the amount of lime up to 25% of the weight of the seeds. It was, however, found that by the lime process the separation of the alkaloids from the extract was difficult. With 40% methylated spirit the alkaloids could be separated easily.

Mixtures of Strychnine and Brucine have been isolated and the separation of the alkaloids is in progress.

240. Extraction of cellulose from rice straw.

M. S. PATEL and B. B. SARDESHPANDE, Bombay.

The object of the present work is to obtain proper data as to the yield of cellulose from Bombay rice straw under various conditions of alkali concentration, temperature and time of digestion and to find out whether it is possible to prepare paper and allied products from the cellulose obtained from Bombay rice straw.

The results can be summarised as follows :—

(1) The moisture content of the rice straw varies with the atmospheric conditions. It is highest in the rainy season. Bombay rice straw contains 48 to 55% total celluloses. Out of this 34 to 37% is alpha cellulose and the rest beta and gamma celluloses.

(2) The liquors obtained after the separation of the first and the second groups stains a bleached piece of cloth. The stain is not capable of being removed even by bleaching.

(3) In actual mill produce the yield of cellulose from Bombay rice straw should be about 36 to 37%.

(4) 140°C is about the best temperature for the digestion of the straw.

(5) For the production of fairly good cellulose the concentration of the alkali ought to be much higher than the 3%.

(6) Under proper conditions of temperature and alkali concentration the period of digestion should be about 1½ hours.

(7) Total alkali required for complete digestion of the Bombay rice straw is 10.5%.

(8) Total amount of bleaching powder required for the bleaching of the cellulose is 4.5% calculated as  $\text{CaOCl}_2$ .

(9) The fibres of rice straw resemble those of esparto in many respects. The cellulose obtained from rice straw is quite suitable for the manufacture of paper and allied products.

(10) As the fibres of rice straw are shorter in length they have to be mixed with a small percentage of cellulose with longer fibres for ordinary paper making purposes.

Samples of paper have been prepared from the cellulose obtained during the investigation and these have been favourably reported upon by paper-makers.



### 241. Preparation of alumina and aluminium sulphate, from Indian bauxite.

M. S. PATEL and G. K. OGALE, Bombay.

Indian bauxite contains a considerable amount of silica and titanium in addition to iron. Both these impurities prevent the profitable extraction of  $\text{Al}_2\text{O}_3$  from Indian bauxite by the Bayer process. The present investigation is undertaken to find out a suitable economic process for the preparation of alumina or aluminium sulphate or both from Indian bauxite. Samples of bauxite have been analysed. One sample having the following composition is being investigated :—

$\text{Al}_2\text{O}_3$	..	..	56%
$\text{Fe}_2\text{O}_3$	..	..	8.5%
$\text{TiO}_2$ ..	..	..	6.5%
$\text{SiO}_2$ ..	..	..	5%

Solubility of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  in acids is being determined under various conditions. It has been found that heating the bauxite at  $110^\circ\text{C}$  for 1 hour prior to treatment increases the solubility of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  in  $\text{HCl}$  and decreases that of  $\text{Al}_2\text{O}_3$  in the same acid.

### 242. Extraction of sodium carbonate and sodium bicarbonate from efflorescent natural soda.

M. S. PATEL and P. S. RAO, Bombay.

Efflorescent natural soda is produced at various localities in this presidency which is utilised for the manufacture of soap by crude methods. This investigation has been undertaken to work out sufficient data to enable one to evolve a suitable process by which Sodium carbonate and bicarbonate can be extracted from the natural soda by simple and economic means.

Samples of natural soda have been collected and analysed. They are found to contain :—

Sample.	$\text{Na}_2\text{CO}_3$	$\text{NaHCO}_3$	$\text{NaCl}$	$\text{Na}_2\text{SO}_4$	Insoluble residue.
(A) Prantij ..	25.66%	4.22%	1.65%	..	69.9%
(B) Kapadvanj ..	20.54%	..	2.19%	..	78.8%
(C) Bhavanagar ..	12.11%	6.73%	..	..	81.5%
(D) Sindh ..	15%	9.3%	8.7%	7.5%	59.7%

The study of the solubility of the following two systems has been undertaken.

- (1)  $\text{Na}_2\text{CO}_3$   $\text{NaHCO}_3$   $\text{NaCl}$   $\text{Na}_2\text{SO}_4$
- (2) " " " —

Equilibrium has been determined at  $29^\circ$ ,  $33^\circ$ ,  $40^\circ$ ,  $60^\circ$ ,  $65^\circ$ , and  $80^\circ\text{C}$ .

The solubility of  $\text{Na}_2\text{CO}_3$  in the presence of the other three salts decreases up to  $40^\circ\text{C}$  and then increases.

The solubility of  $\text{NaHCO}_3$  increases with the rise in temperature.

The solubility of  $\text{Na}_2\text{SO}_4$  decreases up to  $33^\circ\text{C}$  and then increases again.

There is only a slight increase in the solubility of  $\text{NaCl}$  with rise in temperature in presence of the other salts.

### 243. Some new photo-sensitizers.

G. GOPALA RAO, Waltair.

Of the oxides, only zinc oxide has so far been described to possess marked photo-sensitizing activity. It is now found that ignited cadmium



oxide and titanium dioxide are also powerful photo-sensitizers. Cadmium oxide has been studied in detail. It sensitizes the following reactions in ordinary sunlight:—(1) the decomposition of silver nitrate; (2) the bleaching of various dyes in the presence of glycerine; (3) the formation of hydrogen peroxide from water and air; (4) the oxidation of ammonia and its salts to nitrite; (5) the hydrolytic decomposition and oxidation of various nitrogenous substances like urea, the amides, amines, amino-acid, etc. Titanium dioxide is a powerful photo-sensitizer for reactions 4 and 5.

244. The rôle of sodium sulphite in photographic developers.

G. GOPALA RAO and K. M. PANDALAI, Waltair.

Photographic developing solutions contain one or two reducing substances like metol, pyrogallol, or hydroquinone, and a large amount of sodium sulphite with some sodium carbonate. The part played by sodium sulphite has not yet been adequately explained.

Mortan (Radiation in Chemistry) states that sodium sulphite probably prevents the loss of hydroquinone by atmospheric autoxidation, hence more of the hydroquinone would be available for reducing the silver halides in the presence of sodium sulphite than in its absence. Dhar has suggested that this is an induced reaction. It is here shown that Mortan's view was untenable and that the above one was really an induced reaction, the reduction of silver halides by hydroquinone inducing the reaction between sodium sulphite and silver halides.

245. A new synthesis of methyl rhizonate.

R. C. SHAH, Bombay.

Rhizonic acid obtained as a decomposition product of various lichen acids, is 2-hydroxy-4-methoxy-3 : 6-dimethyl-benzoic acid. The acid and its derivatives have been previously synthesised by methods which are long and difficult. The author has now synthesised methyl rhizonate directly from orcinol which was converted into orsenillic acid by the method of Hoesch (*Ber.*, 1913, 46, 886) through oreylaldehyde and subsequent oxidation of its dicarbomethoxy derivative. Orsenillic acid was converted into its methyl ester by means of diazomethane. Methyl orsenillate when methylated by means of KOH and MeI under proper conditions directly gave methyl rhizonate which is insoluble in dilute alkali and gives a deep violet coloration with ferric chloride.

246. The chemistry of imido-chlorides. Part II. Reaction of benzanilide-imido-chloride with *n*-dimethyl *o*-*m*- and *p*-toluidines in the presence of anhydrous aluminium chloride as condensing agent.

R. C. SHAH and N. B. ITCHHAPORIA, Bombay.

In part I, a new and direct synthesis of *p*-dialkylamino benzophenones by condensation of benzanilide-imido-chlorides with dimethyl- and diethylanilines in presence of anhydrous aluminium chloride has been described (Shah and Chaubal, *J.C.S.*, 1932, p. 650). This reaction has been now extended to dimethyl-*o*-toluidine, dimethyl-*m*-toluidine, and dimethyl-*p*-toluidine in order to establish the general applicability of this convenient synthesis, and to study the influence of substituents in the dialkylaniline.

Shah and Chaubal's original method has been improved upon by the use of dry ether, which has been found to have the valuable property of readily dissolving anhydrous aluminium chloride, in place of carbon



disulphide or benzene, as solvent. The resulting ketones, 3-methyl-4-dimethylamino-benzophenone, 2-methyl-4-dimethylamino-benzophenone and 5-methyl-2-dimethylamino-benzophenone are new, the condensation taking place in the para position to the dimethylamino group in the first two cases and in the ortho-position in the third.

It is interesting to note that 3-methyl-4-dimethylamino-benzophenone easily obtained in the present work from dimethyl-o-toluidine, cannot be prepared by the older method from dimethyl-orthotoluidine benzanilide and phosphorus oxychloride (Meisenheimer, *Annalen*, 1921, 423, 75). Interesting observations have been made regarding the influence of steric hindrance in the condensations and in the formation of the oximes and methiodides of the ketones.

#### 247. The chemistry of imido-chlorides. Part III. A synthesis of quinoline derivatives.

R. C. SHAH and V. R. HEERAMANECK, Bombay.

The formation of a quinoline derivative, ethyl 4-hydroxy-2-phenyl-quinoline-3-carboxylate by heating the condensation product of benzanilide-imido-chloride and ethyl malonate was first observed by Just (*Ber.*, 1886, 19, 149, 161) who studied only a few cases of this kind. A systematic investigation of this reaction is being carried out. The original method of condensation has been improved upon, by the use of two mols. of malonic ester instead of one which increases the yield and the purity of the required mono-condensation product. Ring closure has also been brought about by a new method, viz. by means of sulphuric acid.

The following new compounds have been prepared.

*Ethyl-p-nitro-anil-benzenyl malonate, ethyl-(4-hydroxy-2-p-nitrophenyl-quinoline-3-carboxylate, ethyl-o-chloro-anil-benzenyl malonate, ethyl-4-hydroxy-2-chloro-phenyl-quinoline-3-carboxylate, ethyl-anil-m-nitro-benzenyl-malonate, ethyl-anil-p-nitro-benzenyl malonate, ethyl-4-hydroxy-2-phenyl-6-nitro-quinoline-3-carboxylate, ethyl-4-hydroxy-2-phenyl-8-methyl-quinoline-3-carboxylate, ethyl anil-m-methyl-benzenyl-malonate.*

The work is being continued.

#### 248. A new synthesis of 2 : 4-dihydroxy-benzophenone.

R. C. SHAH and P. R. MEHTA, Bombay.

Benzanilides condense with dimethylaniline in the presence of phosphorus oxychloride to give keto-anils which are readily hydrolysed giving dimethyl-amino-benzophenones (Meisenheimer, *Annalen*, 1921, 423, 75; Shah, Deshpande and Chaubal, *J.C.S.*, 1932, 642).

An attempt to condense benzanilide with resorcinol in the presence of phosphorus oxychloride on similar lines was unsuccessful, the benzanilide remaining unchanged. It has been found however that benzanilide readily condenses with resorcinol with a mixture of phosphorus oxychloride and anhydrous zinc chloride as condensing agent, giving finally 2 : 4-dihydroxy-benzophenone in good yield. The condensation takes place more smoothly and the yield of the ketone is further improved when benzanilide is replaced by benzamide.

The method gives a much better yield of 2 : 4-dihydroxy-benzophenone than the known method in which benzoic acid is condensed with resorcinol with the help of anhydrous zinc chloride. Benzanilide has been similarly condensed with orcinol and  $\beta$ -naphthol. The work is being extended.



249. On the study of polyhalides, Part II. Formation and dissociation of chloro-dibromides, and tribromides of sodium, potassium, strontium, and barium.

S. K. RAY, Calcutta.

In continuation of the previous work (*Jour. Indian Chem Soc.*, 1932, 9, 259.) the formation and dissociation of the polyhalides of sodium, potassium, strontium, and barium have been studied by the freezing point method. The constancy of the value of the equilibrium constants, calculated from the freezing point depressions, conclusively proves the formation of the polyhalides. The actual isolation of the complex polyhalides has been possible in some cases.

250. Induced (slow) and photo-chemical oxidation of glucose in presence of glutathione.

C. C. PALIT and N. R. DHAR, Allahabad.

*Induced (slow) oxidation.*—1. Experiments show that there is more oxidation of glucose in presence of glutathione and sodium phosphate than with phosphate alone, showing that glutathione acts as an inductor in the oxidation of glucose in presence of phosphate and that with a definite amount of glutathione, the amount of oxidation of glucose increases with the increase of phosphate.

2. With sodium bicarbonate, the amount of glucose oxidised is also greater in presence of glutathione than in its absence, but with sodium carbonate and sodium sulphite respectively, the results obtained are quite the reverse. Also there is more oxidation of glucose in presence of sodium carbonate or sodium sulphite alone than in presence of either of these and glutathione together.

*Photo-chemical oxidation in sunlight.*—1. Experiments show that (a) the amount of oxidation of glucose increases with the increase of sodium phosphate, whether the oxidation occurs in presence or absence of glutathione, (b) the amount of oxidation of glucose with phosphate in presence of glutathione is greater than in its absence under similar conditions, and (c) the oxidation of glucose increases as the amount of glutathione increases.

2. In presence of sensitisers such as uranium nitrate, ferric nitrate, zinc oxide, animal charcoal, etc. oxidation of glucose in presence of glutathione is greater than in its absence and the order in which it is oxidised is uranium nitrate > ferric nitrate > zinc oxide > animal charcoal.

3. Photo-chemical oxidation of glucose with sodium bicarbonate is greater in presence of glutathione than in its absence, while with sodium carbonate the results are quite the reverse like the results obtained in case of induced oxidation.













# INDIAN SCIENCE CONGRESS.

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Twentieth Annual Meeting,  
PATNA, 1933.

ABSTRACTS OF PAPERS.

Section of Zoology.

*President :—Prof. R. Gopala Aiyar, M.A., M.Sc.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Zoology.

### Abstracts.

1. Multiplication of Trichomonads by multiple longitudinal splitting or fission.

G. C. CHATTERJEE and A. N. MITRA, Calcutta.

In three previous papers, we have shown that instead of the binary method of division (a trichomonad dividing into two equal halves, each one having all the organelles of the one dividing), which is described as the method of multiplication in all papers on the subject, there is another method of multiplication, in which an adult organism gives origin to numerous minute amoeboid organisms having no flagella, which subsequently develop their organelles. We have since found another method of multiplication which is the subject of this paper, in which an organism possessing all the organelles but very small in size, splits up into innumerable organisms which possess a single flagellum, which develops later on into an ordinary trichomonad. The different stages in the development have been observed from minute ones being not more than 2 or 3 $\mu$  to 18 or 20 $\mu$  or more.

2. Myxosporidia from India.

H. N. RAY, Calcutta.

Several myxosporidia have been studied from fish, amphibia and reptile. Following genera are for the first time recorded from India: *Ceratomyxa*, *Chloromyxum*, and *Zschokkella*.

Life cycle of *Chloromyxum amphipnoui* n. sp., and *Zschokkella prashadi* n. sp., have been dealt with in detail. Fish mortality in a confined area of water due to myxosporidian infection has also been discussed.

3. *Lankesteria culicis* from *Aedes* (*Stegomaya*) *albopictus* in Calcutta.

H. N. RAY, Calcutta.

Historical review of the distribution of *L. culicis* is given. Its life history revised and certain features, such as method of association, chromosome number, and the position of the residual mass in the spore have been found to be worth recording. Occurrence of epimerite has also been discussed.

4. Boring apparatus in *Balantidium*.

H. N. RAY and M. CHAKRAVARTY, Calcutta.

Presence of a boring mechanism in several species of *Balantidium* have been noted. It is suggested that human *Balantidium* may be investigated upon from this point of view.

5. On the trematode found in the liver of *Ophiocephalus striatus*.

T. SUBRAMANYAPILLAI, Bangalore.

The anatomical and embryological study of this trematode seems to suggest that it is a form more allied to *Fasciola hepatica* than to any other



trematode. It agrees with the latter species in all respects except in the position of the genital aperture as well as in the disposition of the gonads. The genital opening is far behind the ventral sucker, almost in the middle of the ventral side. The testes are centrally placed, one behind the other, the anterior one lying just behind the genital opening; and the ovary lies between the two testes. These differences can be reconciled with the conditions existing in *F. hepatica*, if the disposition of the gonads in the pre-adult stage of the parasite, under consideration, is studied. There are indications in this, to show, that the genital aperture was once anteriorly placed in front of the ventral sucker, and that it has shifted back correlated with the need for a greater efficiency of the ventral sucker. This upsets the normal position of the testes, and resulted in a torsion which brought the once right testis to the centre, and the once left testis more forward, and then to the centre, in front of the ovary.

If Biogenetic law can be relied upon, the above facts show that the two trematodes arose from a common ancestral form, whose permanent host was a fish and the intermediate host a water-snail. The ancestral cercariae must have evolved along two lines, one showing a tendency for securing a terrestrial vertebrate host; the one that remained in a Piscian host became more specialised and diverged from the ancestral form, whereas the other kept up much of its ancestral traits.

#### 6. On a new trematode of the genus *Astiotrema* Looss, 1900, from the intestine of a tortoise, *Chitra Indica*.

G. S. THAPAR, Lucknow.

The genus *Astiotrema* was erected by Looss in 1900 for the reception of two species, *Distomum reniferum* and *Astia Impleta*. Subsequently several other species have been added to the genus. The present paper adds another species, *Astiotrema indica* n. sp., to the genus in question.

The specimens were obtained from the intestine of *Chitra Indica* from the river Gomti and present the following characters:—

1. Spherical ovary in front of the testes.
2. The testes are lobed 9-10 lobes in each.
3. Receptaculum seminis is large, semilunar in shape, transversely disposed across the body.
4. The cirrus is very characteristic and forms a definite coil in its course.

A detailed account of the anatomy of the trematode is given. The paper concludes with discussion on the status of the subfamily Astiotreminae Baer, 1924, and in the light of the recent researches, gives an amended definition of this subfamily.

#### 7. On the morphology of *Discocotyle Sagittatum*.

G. S. THAPAR and M. B. LAL, Lucknow.

In the course of his investigations on the helminth parasites of fishes that died in the aquarium of the London Zoological Society, the senior author found a very heavy infection in the gills of salmon trouts by these parasites. The excretory system was there examined in fresh specimens and the other details in the anatomy are now studied by both of us from a series of prepared slides.

The genus *Discocotyle* has been studied by several earlier workers but the following interesting features are now being recorded:—

1. The division of the body into three regions—the large middle region being the sexual region of the animal.
2. The branched diverticula of the intestine.
3. The peculiarities and details in the excretory system appearing to connect Monogenea and Digenea together.



4. The peculiar anchoring process at one end of the egg.

A detailed account of the anatomy, particularly of the excretory and reproductive systems, is given in the paper.

8. On the morphology of a new trematode from Golden orfe.

G. S. THAPAR and J. DAYAL, Lucknow.

A large number of trematodes were collected from the intestine of Golden orfe and they present the following distinguishing characters :—

1. Presence of armed genital sucker anterior to the acetabulum.
2. Diagonal and lobed testes.
3. The lobed ovary in between the two testes.
4. Coiled uterus lying between the acetabulum and the posterior testes.

A detailed account of the anatomy of the animal is given. The paper concludes with a discussion on the systematic position of the animal. It appears to be closely allied to the genus *Sphærostoma*, but differs from it in several important features which necessitate the creation of a new genus for the present form.

9. On the morphology and systematic position of *Cephalogonimus* and *magnus* n. sp. from *Trionyx gangeticus*.

B. B. SINHA, Lucknow.

A large number of specimens were obtained from the intestine of *Trionyx gangeticus* at Lucknow. The chief peculiarities are :—

1. Anterior half of the body is covered over with spines.
2. Oesophagus is as big as the muscular pharynx.
3. The excretory vesicle is longer than the arms of 'Y'.
4. The uterus completely fills the posterior part of the body and can be distinguished into ascending and descending rami.
5. The yolk-glands are in the middle third of the body, extending beyond the posterior margin of the acetabulum.
6. An elongated, flask-shaped cirrus-sac with a long, narrow neck is present.

The new species differs from other members of the genus in its larger size and in the extent of the vitellaria.

The paper concludes with a discussion on the systematic position of *Prosthogonimus*—which has recently been included in the family Lepodermatidæ by Poche (1925). The author has argued for the exclusion of *Prosthogonimus* from the family Lepodermatidæ and has advanced his arguments in favour of its inclusion under the family Cephalogonimidæ along with the genus *Cephalogonimus*.

10. Notes on the occurrence and external features of a fresh-water poly-chæte.

C. BAL, Benares.

A poly-chæte worm was found swimming freely in river Ganges close to the Ghats at Benares.

Two species of poly-chæte *Matla bengalensis* Stephenson (1908, 1910) and *Spio bengalensis* Willey (1908) have been recorded previously from Port Canning (Gangetic Delta), but none so far was found to occur up the river beyond this. The occurrence of a poly-chæte about 500 miles up the stream from the delta is noteworthy.

The question of the distribution of poly-chætes in fresh and brackish water has been briefly discussed.



Only one specimen of this species could be collected and the anterior region was unfortunately mutilated. It could not, therefore, be identified. An attempt, however, is being made to collect more specimens of this species.

The structure of parapodium and various types of Setæ has been given. The worm possesses branchiæ.

# 11. An account of the development of *Diapatra Variabilis* (Southern).

G. KRISHNAN, Madras.

The development from the atrochal stage to a period when most of the adult structures have been formed, is described. The larvæ were reared in the laboratory. The fertilized eggs occur in masses inside the tubes of the parents. They are heavily yolked, and the larval history is much abbreviated. There is no free swimming phase, and the early development takes place inside the tube, the young leaving it with several pairs of parapodia. The tentacles, anal cirri, the jaws, and the branchiæ appear comparatively early before the worm develops about 10 to 11 parapodia. The cilia are reduced. The true compound setæ are absent. The sequence of appearance of setæ is described. The tube-forming habits are also described. A comparison is made with the development of *Diapatra cuprea*.

# 12. On the physiological significance of the enteronephric type of nephridial system found in Indian earthworms.

K. N. BAHL, Lucknow.

During the years 1919-1926, the author described the 'enteronephric' type of nephridial system in earthworms belonging to the genera—*Pheretima*, *Lampito*, and *Woodwardia*. In all these genera, the nephridia discharge their excretion into the intestine instead of one to the surface of the body. It was further suggested that the basis of classification of nephridia should be the place of their opening rather than their size; Stephenson in his recent monograph on the Oligochaeta has accepted this suggestion and classified the nephridia into 'exonephric' and 'enteronephric' types.

The question of the physiological significance of these 'enteronephric' nephridia still remains open although it was suggested in 1919 that the enteronephric system was possibly an adaptation for the conservation of moisture in a dry climate. In the present paper, the author has compared the habits of *Pheretima* with those of *Eutyphæus*, the former possessing enteronephria and the latter exonephridia. He has, next, compared the castings of these two worms in respect of their shape and consistency, which go to prove that his suggestion is correct. Finally, he has given data with regard to the percentages of moisture present in the castings of these two kinds of worms. In all the five experiments made, the percentage moisture was higher in the castings of *Eutyphæus* than in those of *Pheretima* proving conclusively that the gut of *Pheretima* absorbs the water from the excretory fluid and conserves it for the needs of the worm.

# 13. The larval stages of *Acetes* sp.

M. KRISHNA MENON, Madras.

A fairly complete account of the larval development from the earliest free-swimming stage up to one in which the animal, in all essential respects, has acquired the adult characters is given. In all nine stages have been



studied. There are three protozoëa and two mysis stages. The development of the full number of pleopods is an extremely slow process. The development shows many interesting features of resemblance to the developments of *sergestis*, *Petalidium*, and *Lucifer* of the same family.

14. Distinctive characters of the larval development of *Callianassa* sp.

M. KRISHNA MENON, Madras.

The development of this species of *Callianassa* differs considerably from those of all other species of the genus so far studied. One of the most important differences is the abbreviation of larval life, there being only two stages. The mouth appendages, abdominal somites, and telson of these show important variation from those of the corresponding stages of other species of *Callianassa*. On the other hand, in the shortness of larval life, in the nature of the telson, and in the absence of uropods during this period this form resembles the development of the genus *Axius*.

15. The larval development of *Gebiopsis* sp.

M. KRISHNA MENON, Madras.

There are five larval stages in the development of this species whereas most of the other species of Upogebinae, the developments of which have been studied, pass through only four stages, and in some cases only three. The present form differs from the others in several other important respects also, as for instance, in the presence of lateral spines in the abdomen, and in the very late appearance of the median spine in the posterior edge of the telson.

16. Development and habits of *Hippa asiatica*.

M. KRISHNA MENON, Madras.

Larvæ of *Hippa* are very common in the plankton in all except the hottest months. There are five free-swimming larval stages. They resemble very closely to those of the American species, *H. emerita* (talpoida), the first stage of which was described by Faxon, and the last three stages by S. I. Smith. The two species differ, however, in respect of the disappearance and reappearance of the abdominal appendages in their post-larval life.

17. Yolk formation in *paratalphusa hydrodromus*.

A. NARAYAN RAO, Bangalore.

On examining a series of sections of the ovary of this freshwater crab prepared by Osmic technique the author has observed that the formation of fatty yolk by the Golgi vesicles is in accordance with the findings of Nath (*Q.J.M.S.*, Vol. 74, No. 296). While the albuminous yolk could be traced to Mitochondria, an observation which is in accordance with the findings of King (*P.R.S.*, Vol. 100, No. 700). Nowhere in his own preparations the author could discover the nucleolar extrusions which, according to Nath, are the active agents in the formation of albuminous yolk. The paper further discusses the collateral problems arising from these observations.



18. A short review of the Myriapod collection in the Indian Museum, Calcutta.

M. B. LAL, Lucknow.

The present paper is the outcome of the author's short stay in Calcutta during the summer of 1930 when he had the opportunity of examining the Myriapod collection in the Indian Museum.

The collection is very useful though by no means rich, as either the coastal regions or some hilly places have been explored; while very little collection has been made from the interior of the country.

For the purpose of showing clearly the extent of exploration for the collection of Myriapods, the author has given about a dozen outline maps of India, Burma, and Ceylon, and located the places from which collections have been made. A glance at the maps gives an idea of the immense work lying before the Zoologists for the study of this group as no collections have been made from vast stretches of the country.

The author has also collected and located some forms of Diplopoda (millipedes) which were not in the museum collection. A detailed list of the genera and species, together with their places of collection, is also given.

19. Preliminary notes on the copulation, fertilisation, and egg-laying of the millipede, *Thyropygus malayus*.

M. B. LAL, Lucknow.

Bhatia and Choudhary (1927) described copulation in this millipede, though under a wrong name of *Spirostreptus* Brandt., but their observations seem to be both scanty and inaccurate. The millipedes have been identified as *Thyropygus malayus* and complete and detailed observations are recorded in this paper.

The following important points may be noted in this connection:—

1. Copulation lasts as long as 20 to 40 minutes if the animals are left undisturbed.

2. The animals, while copulating, do not separate if carefully handled, though even the slightest sound vibrations, e.g. tapping of the table on which the dish containing the animals is kept, disturbs them.

3. There is a period of excitement for the male after which it never likes to copulate.

4. There is a jerking movement every 3 or 4 minutes by which the Gonopods press firmly against the vaginal discs, and this movement is very much pronounced at the end of the copulating process after which the animals separate.

5. Copulation is generally observed in nature from July to November. Copulation ceases during the winter months when the animals hibernate.

6. Eggs may be laid on the third day after the last copulation, or as late as 5 to 9 or even 13 days after.

7. Eggs do not develop if even slightly exposed to air, hence eggs are laid singly in small egg-capsules of earth which serves for protection during development. As many as 31 egg-capsules were collected from a single female.

20. On the chemical nature and physiological significance of the so-called 'Stink-glands' of *Thyropygus malayus*.

M. B. LAL, Lucknow.

These glands lie on the lateral walls of the chitinous body rings but are absent from the first five segments, including collum, and from the last or anal segment. They open outside as longitudinal slits through



which comes out a yellowish pungent fluid when the animals are handled. On irritation, however, the animals pour out considerable quantities of this fluid.

Microchemical tests were applied for detection of Hydrocyanic acid which is present in exceedingly small quantities. The author has also been able to detect minute quantities of free chlorine in the secretion.

The probable function of the glands is protective. Millipedes are quite unpalatable due to this fluid and very rarely preyed upon and eaten. Secondly, the hydrocyanic acid and free chlorine act as a sort of disinfectant and keep the surrounding soil and decaying vegetable matter where the animal lives free from bacteria and other micro-organisms.

Quantitative estimation of chlorine and hydrocyanic acid is being carried out. Details of the experiments are given in the paper.

## 21. On the egg-laying in *Strongylosoma* and *Orthomorpha*.

M. B. LAL, Lucknow.

Several local millipedes were collected and kept in laboratory under observation. Eggs were laid in clusters and in small pits in the soil. Egg-laying begins in early rains as soon as the animals come up on the surface. In *Strongylosoma contortipes* Attem., the number of eggs varied from 127 to 185 with different individuals. Eggs are red in colour. In another variety of *Strongylosoma*, viz. *Strongylosoma contortipes*—Forma minor—eggs varied from 78 to 93 in number and are pale yellow in colour; while in *Orthomorpha modestine* Silv., eggs are absolutely white and numbered from 38 to 60 with different individuals.

## 22. On the faecal pellets of millipedes.

M. B. LAL, Lucknow.

The millipedes are mainly vegetable feeders but they also swallow considerable quantity of earth along with their food, which they pass out in form of small beads. These faecal pellets resemble more or less the castings of *Pheretima*. They measure 5 mm. in length, and 1 to 2 mm. in width in case of *Thyropygus Malayus*, but they are as small as mustard seeds in case of smaller millipedes. Swallowing of earth is done during burrowing when the Labrum works like a spade and though the feet help in throwing the earth backwards still a lot is engulfed.

## 23. Notes on some Indian Thysanoptera with brief descriptions of new species.

T. V. RAMAKRISHNA AYYAR, Coimbatore.

This paper includes the results of the author's recent studies on the systematics and bionomics of some Indian Thysanoptera, and forms a supplement to them. Part of the material on which the present study is based was collected from sandal wood trees growing in the important sandal areas of Coorg and Salem by officers of the Imperial and Madras Forest Departments. The study of sandal 'thrips' forms a part of the investigation of the complete insect fauna of this valuable tree undertaken in connection with the 'sandal spike' which is believed by some scientists to be an insect-borne virus disease causing loss to the extent of over five lakhs of rupees per annum. It may also be added that such a faunistic work would represent the first intensive study of the insect fauna of a single species of forest tree in the Indo-Malayan region, and this would undoubtedly form a substantial contribution to our knowledge of the fauna of South India. The rest of the material includes



collections made by the author and others from the different parts of the country both on sandal and other host plants.

Of the following two dozen insects noted in the paper, eight happen to be species new to science and five are forms not previously recorded from India. Eleven species are from material collected on sandal wood tree and of these, two are extremely interesting giant forms new to science. Short notes on the different forms and very short descriptions of the new species make up the major portion of this paper.

#### SPECIES NOTED :

1. Erythrothrips asiaticus, R. and M.
2. Hemianaphothrips palmæ, n. sp.
3. Pseudodendrothrips ornatissimus, Schm.
4. Parthenothrips dracænæ, H.
5. Heliothrips indicus, Bag.
6. Thrips florum, Schm.
7. Tæniothrips chætogastra, n. sp.
8. Panchætothrips indicus, Bag.
9. Ecacanthothrips fletcheri, n. sp.
10. Liothrips dampfyi, Ky.
11. Haplothrips inquilinus, Pr.
12. H. Ganglbaueri, Schm.
13. Trybomiella ramakrishnæ, Ky.
14. Dolichothrips indicus, H.
15. Karnyothrips nigriflavus, n. sp.
16. Androthrips coimbatorensis, n. sp.
17. Ramakrishnaiella nirmalapaksha, R. and V.
18. Mallothrips indica, Ramkr.
19. Dinothrips sumatrensis, Bag.
20. Elaphrothrips beelsoni, n. sp.
21. E. chandana, n. sp.
22. Neosmerinthothrips fructum, Schm.
23. Kleothrips gigans, Schm.
24. Idolothrips tungabhadrae, n. sp.

24. A note on the gut and nervous system of the adult female lac insect *Laccifer lacca*, Kerr (Coccidæ).

P. S. NEGI, Namkum.

The internal anatomy of the female lac insect is a much neglected subject. Dr. A. B. Misra in his papers 'On the post-embryonic development of the lac insect' and 'On the internal anatomy of the female lac insect', has erred in his observations and mistaken the *Consolidated ventral ganglia* for the pharynx, and has stated that the nervous system is broken into separate parts. The paper disproves these observations of Dr. Misra, and states that the pharynx is only slightly bigger in diameter than the œsophagus. The bunch of salivary glands of either side with its common duct is closely attached to the consolidated ventral ganglia. The disposition of the gut is not materially affected by the distortion of the shape of the lac insect, and 'the free ends of the malpighian tubes and the blind end of the recurrent intestine' are directed towards the posterior end of the insect.

The nervous system is continuous and not broken into separate parts. It consists of the Cerebral ganglia; the connectives join to form the consolidated ventral ganglia which gives nerves to the anterior parts and continues posteriorly into the nerve chord for a short distance; the nerve chord then divides into two main branches which divide and subdivide to supply the various posterior parts of the female.



25. Anatomy of the worker ant *Dorylus orientalis*.

D. MUKERJI, Calcutta.

The writer showed the phylogenetic affinities of the Dorylinae to the vespoid on the basis of the internal anatomy of the male ant *Dorylus* (*J.A.S.B.*, XXII, 1927). In the present paper the internal anatomy of the blind worker ant *Dorylus orientalis* is investigated. The existence of well-developed ovaries in a few of the major workers and presence of air sacs in the workers which are non-winged as in other examples of ant of peculiar in leading a subterranean and nomadic life, deserve special mention. The workers are carnivorous and not vegetable feeders as reported by previous authors. The max-palp is one jointed and not two.

## 26. Notes on the bionomics and rearing technique in the study of a Eulophid parasite.

K. P. ANANTANARAYANAN, Coimbatore.

In India, so far as the writer is aware, very little has been done with regard to the details on the life history and the technique of rearing of Hymenopterous insects belonging to the group of chalcid flies though it is long recognised that they are one of the most numerous and useful of the groups of insects. The present paper is an attempt in this direction, based on the writer's observations on a parasite of the Hymenopterous family which the writer had the opportunity to rear in large numbers for the control of the coconut caterpillar in Malabar, during the past five years.

In this paper are included the details as to the life history and habits of the parasite, the rearing technique in the laboratory, and the results of the preliminary investigations on the influence of weather on the breeding of the parasite, together with the work of the insect in nature.

This Eulophid is one of the important parasites indigenous to Malabar, and found comparatively the most efficient of the natural enemies of the coconut caterpillar for utilising it as a method of biological control. It may be added that the details with regard to the life history and habits of this parasite on coconut caterpillar have not been recorded before.

## 27. The termites of Orissa, their behaviour, and some effective methods of prevention.

S. K. GHOSE, Cuttack.

Affecting buildings, the author describes in detail the survey of termites found in Orissa, and gives a critical review of their behaviour and systematy.

The preventive measures suggested are bound up with the use of arsenic in the foundation of buildings, pitch and cement in the walls and floors, and reinforced concrete in place of woodwork, and special treatment of wooden material.

The economic aspect of the problem is dealt with.

A collection of termites obtained from different parts of Orissa will be exhibited in the meeting.

28. On the habitat of the *Maruina*-type of Psychodid larvæ in India (insecta : Diptera).

S. L. HORA, Calcutta.

The *Maruina*-type of Psychodid larvæ resemble superficially the larvæ of the Blepharoceridæ and, like them, are provided with a row



of (6 to 8) ventral suckers. The Blepharoceridæ live in swift currents adhering to smooth rocks and boulders; whereas the '*Maruina*' larvæ live round waterfalls on rocks, stones, and pebble which are either constantly washed by spray or moistened by dripping water from above. They avoid strong currents and live either entirely out of water or in shallow, gentle currents at the sides of torrential streams. They have been found in India at Dalhousie in the Western Himalayas and in streams near Teesta Bridge below Darjeeling. The present note is written with a desire to direct the attention of future collectors to the type of habitat in which to look for them in this country. The structural peculiarities of these larvæ and their evolutionary significance are indicated. From the known distribution of such archaic forms as *Deuterophlebia*, *Maruina*, and the Blepharoceridæ it is suggested that they may have evolved independently on different continents under the influence of a set of same or similar environmental factors.

Notes are given on the methods of collecting and rearing these interesting flies.

## 29. On the Cytoplasmic inclusions in the oogenesis of *Periplaneta americana* (Linn.).

V. D. RANADE, Allahabad.

The oogenesis of *Periplaneta americana* (Linn.) has been studied both by intra-vitam examination and fixed preparations. Centrifuge experiments have also been carried out.

In the oocytes treated with dilute neutral red for about 20 minutes, the vacuome is tinged red and generally becomes prominent. In the earlier oocytes there are one or two patches of vacuome consisting of about five or six discrete round bodies. With the growth of the oocyte these patches increase in number and are uniformly distributed throughout the oocyte. In an advanced oocyte separate discrete vacuome are also clearly visible among the large and prominent patches of vacuome.

The Golgi vacuoles are not stained by neutral red and appear as refractory bodies which on the introduction of 2% osmic acid under the cover-slip clearly show the osmiophilic rim around a colourless core. In the oocytes treated only with 2% osmic acid for 20 minutes the vesicular Golgi bodies with chromophilic rim and chromophobic core are clearly seen. There are also some crescent-shaped Golgi bodies. In the youngest oocyte the Golgi bodies aggregate in a juxtannuclear position forming the yolk-nucleus of Balbiani. From now onwards they distribute in Cytoplasm in patches. With the growth of the oocyte, the Golgi bodies grow in size and begin to deposit fat in their central core and become converted into fatty yolk bodies. Precisely similar stages of the growth and the dispersal of the Golgi bodies were also observed in the fixed preparations. Golgi bodies are also derived from the follicular epithelium cells of the oocyte by the process of 'infiltration'. Golgi bodies make their appearance after prolonged treatment (25 minutes) with Janus green B in the intra-vitam examination.

In the oocytes treated with a dilute solution of Janus green B for 10 minutes the mitochondria are seen as fine granular bodies. There are also present baton-shaped mitochondria, some of which may be seen breaking into granular mitochondria. In the youngest oocyte they are aggregated in the juxtannuclear position to form the yolk nucleus of Balbiani. In the advanced oocytes they are distributed in patches, and ultimately they get evenly distributed in the Cytoplasm as granular bodies. Mitochondria, like the Golgi bodies, swell up and directly give rise to albuminous yolk. There is no evidence of nucleolar extrusions in the solid form.



30. Spermatogenesis in *Orthacris* (acrididæ).

T. RAMACHANDRA RAO, Bangalore.

The paper deals mainly with the chromosomes and their behaviour in the male germ cells of *Orthacris* sp. of the subfamily Pyrgomorphinæ. There are 19 chromosomes made up of 9 pairs of homologous chromosomes and the odd X-element. While ordinarily the form of all these chromosomes is uniform. In one of the individuals studied there occurs regularly in all the nuclei of the first spermatocyte metaphase, a J-shaped tetrad due to the presence of a pair of heteromorphous homologues.

The process of synopsis and related phenomena are described in detail, and are found to resemble in main outline the same phenomena in *Mecostethus* (McClung, 1927). Indications of the presynaptic split and the precocious behaviour of the X-element are clearly described. Certain differences are however noted. Even a close examination does not reveal the presence of protoplasmic processes between adjacent cells during diakinesis. An attempt is made to study the segregation of the unequal homologues in relation to the sex chromosomes. The rôle of centrioles in sperm formation is briefly outlined.

A comparative study of these processes in *Aularches miliaris* (Linn.) is also made.

31. A note on Gude's classification of *Cyclotopsis*.

R. V. SESHAIYA, Annamalai Nagar.

The paper points out the incorrectness of Gude's inclusion (*Fauna of British India-Mollusca*, Vol. II) of the genus of *Cyclotopsis* in the family of Cyclophoridae. An examination of *Cyclosopsis subdiscoidea* (Sowerby.) shows the characteristic features of Potamiasidae (=Cyclostomatidae) in (1) the presence of a deep longitudinal pedal groove, (2) the concentration of the pedal centres, (3) the presence of a single otolith in the otocyst, (4) the structure of the reproductive system, (5) the structure of the radula, and (6) the absence of jaws.

32. Anatomy of *Paludomus tanschaurica* (Gmelin).

R. V. SESHAIYA, Annamalai Nagar.

The paper gives a preliminary account of the anatomy of *Paludomus*. Among other features, it describes the oligopyrene and eupyrene types of sperms found in the species, the peculiarities in the pallial circulation and the function of the marginal processes of the mantle. A definite blood-sinus corresponding to the 'vena circularis' of Pulmonates is present in the anterior part of the mantle. A sinus of this type does not seem to have been recorded till now in any of the aquatic Prosobranchs. The 'vena circularis' of *Paludomus* receives venous blood from definite sinuses in the marginal processes of the mantle. From the 'Vena circularis', the blood flows through ramifications on the left side of the mantle into the efferent ctenidial vein. The marginal processes seem to serve as accessory respiratory organs.

33. A note on the mucous glands in the foot of *Ariophanta*.

T. K. GOPALACHARI, Cocanada.

(Communicated by Mr. R. V. Seshaiya.)

The paper gives an account of the different types of mucus-secreting glands found in the foot of *Ariophanta*.



34. The spicules and their variation in *Salmacis bicolor* and *Stompneustes variolaris*.

M. KRISHNA MENON and R. GOPALA AIYAR, Madras.

The paper deals with the occurrence and distribution of spicules in *Salmacis bicolor* and *Stomopneustes variolaris*. Spicules are described in *Salmacis bicolor* from the gonads, the reproductive ducts, coelomic epithelium, alimentary canal, tube feet, ordinary and buccal, buccal membrane, stone canal, axial sinus and gills. The spicules are of two varieties both belonging to the bihamate type. Variations are common in the spicules from the gonad, but absent in the other portions of the body. The percentage of variation is noted. A detailed description of the spicules in various regions of the body is given. An attempt has been made to note if there is any relation between the size of the spicules and the size of the individual.

In *Stomopneustes variolaris* in spite of its otherwise robust appearance spicules are conspicuous by their poor development. The bihamate type is absent. The gonads do not contain any spicules amongst the germ cells. But the membrane surrounding the gonad often possesses spicules of an irregular type. In the alimentary canal in the beginning and the end scattered triradiate spicules are observed. The perforated plates of the tube feet are described. The buccal membrane and gills also contain scattered plates of a similar nature.

35. On certain hitherto unknown characters in the Fam. Notopteridæ.

M. RAHIMULLAH and B. K. DAS, Hyderabad.

So far only two distinct species of the genus *Notopterus* have been recognised as known to be distributed practically all over India. Their taxonomic position depends upon the following characters:—

1. The presence or absence of a concavity over the upper profile of the head.
2. The presence or absence of the serrations towards the lower edge of the preorbital.
3. The variation in the number of serrations along the abdominal edge between the throat and the insertion of the ventral fins.
4. The number of dermatrichia in the continuous anal and the caudal fins.
5. The extension of the maxilla in relation to the orbit.
6. The position of the dorsal fin.

Comparing the data given for the species of *Notopterus* in the *Fauna of British India*, 'Fishes' with those of the specimens (more than four dozens examined), obtained from the river Mûsi which present several variations and new characters, the following points are worthy of mention:

- (a) B. VII.                      D. 8-10.                      P. 14-15.                      V. 5.  
       A. 99-102.                  C. 10-13.                      Ll. 180

(b) Concavity over the dorsal surface of the head quite prominent.

(c) Serrations existing along the lower surface of the Preorbital.

(d) 28-31 serrations along the abdominal edge.

(e)  $A + C = (95-102) + (10-13)$ .

(f) Extension of Maxilla ventrally =  $\frac{1}{2}$  to  $\frac{3}{4}$  of the diameter of the orbit.

(g) Dorsal fin commences much nearer the tail than to snout.

Taking all the facts into consideration the authors find that the problematical type of *Notopterus* embraces the characters of both the species of the genus *Notopterus*. It comes more or less near to *kapirat* in the following respects:—



- (i) Composition of the caudal fin.
- (ii) Composition of the anal fin.
- (iii) Serrations present along the ventral surface of the Preorbital.

Further details of similarity and differences, etc. are given in the paper.

In the opinion of the authors this seemingly new group of fishes of the genus *Notopterus* forms what might be called a *local race*, as if emerging from the almost cosmopolitan stock of *kapirot*. To be brief, in some respects they possess certain characters which are undoubtedly intermediate between those of *kapirot* and *chitala*, while in other respects they are widely different from either of them.

### 36. Observations on the confluence of the median fins in one of the common cat-fishes of the Nizam's Dominions, Mároof (Mahgur or Mângri—*Clarias batrachus*).

M. RAHIMULLAH and B. K. DAS, Hyderabad.

Confluence of the median fins has been noted and studied in two examples of the Cat-fish, Mároof (*Clarias batrachus*).

(a) In the first case :

- (i) All the three vertical fins (dorsal, caudal, and anal) are confluent with one another; that is to say, they form one continuous vertical fin-fold.

$$D + C + A = 80 \text{ rays.}$$

- (ii) The primary caudal fin (homocercal) is severed off, probably due to certain accidental causes, and in its place a new tail-fin is regenerated as a secondary acquisition round the much abbreviated caudal axis.
- (iii) The endoskeleton in this case is very much modified: no trace of the urostyle and the hypurals—the terminal part of the vertebral column is slightly deflected upwards. All the dermatrichia of the last portion of the anal as well as the dorsal fins bend towards and encircle round the caudal axis.

(b) In the second case :

- (i) Only the dorsal and the caudal fins are united together, this condition being intermediate in form between the first case and the normal type.

$$D + C = 73$$

$$\downarrow$$

$$73 + A = 118 \text{ rays.}$$

Normal type:  $D + C + A$  (all fins though quite separate and independent of one another) = 122 rays.

- (ii) The original homocercal caudal fin is retained, but there is a single much abbreviated hypural bone (as compared with a large, partly coalesced, vertically-directed, fan-shaped bony plate formed by the fusion of six hypurals in a normal type) supporting the whole of the spread-out hypochordal dermatrichia—five of the hindmost dermatrichia of the dorsal fin being crowded together and situated over the upper corner of the single hypural bone, and are thus enclosed within the common fin-fold.

(c) The dermatrichia in both the first and the second cases are abbreviated.

(d) The number of vertebrae in the caudal and the abdominal regions of the vertebral column in the first, second, and the normal cases



are 24 and 18 (=42), 35 and 19 (=54) and 36-37 and 18 (=54-55) respectively. This clearly shows that the vertebral elements in the first case are nearly  $\frac{2}{3}$  of those of the normal type.

(e) In certain fishes the median fins may be very rudimentary (symbranchidæ); imperfectly or well developed in Elasmobranchs and other bony fishes. Dorsal fins may be normally confluent with the caudal (*Chaca lophioides*), or all the three vertical fins might be united together as in *Plotosus*. In a few other Indian fishes the caudal fin is united with the anal (*Callichrous*, *Coila*, *Notopterus*, etc.). Other cases where the confluence of all the three median fins exists are: Murænidæ, Gobioides, Trypauchen, Cepola, certain Rhynchobdellids, most Ophiidæ, a few Pleuronectids, Dipnoi, etc.

### 37. On the hypobranchial artery of *Labeo calbasu* (H.B.) and *Mugil corsula* (H.B.).

E. GHOSH, Calcutta.

*Labeo calbasu*.—The hypobranchial artery arises from the first and second efferent branchial vessels of the left or of right side, or of both sides, the mode of origin in the last case being similar to that in *Cirrhinus mrigala* and *Calla calla*. The artery passes backwards along the right or left side of the ventral aspect of the ventral aorta. It ends in the ventral aorta just beyond its origin from the bulbus arteriosus. Branches are given to the urohyal region, pectoral region, and to the pericardium. The bulbus arteriosus is produced into two lateral, elongately triangular diverticula. Efferent branchial vessels arise separately. First and second efferent branchials unite to form the first epibranchials which fuse to form the dorsal aorta. The third and fourth efferent branchials fuse to form the second epibranchials which open into the dorsal aorta.

*Mugil corsula* (H.B.).—The hypobranchial artery arises from the second pair of efferent branchial vessels and also receives the third pair of efferent branchials. It does not supply the heart, but is continued to the pectoral region, giving branches to the urohyal region. The ventricle is elongated and its apex overlaps the bulbus arteriosus on the ventral aspect in the form of a rounded sac. The first three pairs of efferent branchial vessels arise at equal distances from one another. The fourth pair arise immediately behind the third from the ventro-lateral aspect of the ventral aorta. The first two efferent branchials unite to form the first epibranchial which runs backwards in a widely S-shaped curve and unites with its fellow of the opposite side to form the dorsal aorta. The third and fourth efferent branchials unite to form the second epibranchial which ends in the dorsal aorta. There are two slender accessory efferent branchial vessels from the third and fourth gills which unite to form a common trunk ending in the dorsal aorta immediately in front of the second epibranchial artery.

### 38. Studies on the Asphyxiation of some air-breathing fishes of Bengal.

E. GHOSH, Calcutta.

The study of the mode of respiration in air-breathing fishes has already been made by Rev. Boake, Day, Dobson and Das, who devised experiments so as to prevent access to free air. The results were that the fishes died of asphyxiation after certain periods which varied in different cases. The experiments are repeated here. It is found that the periods of death are in all cases lengthened out. Conclusions: (1) The shorter period in the previous experiments was due to asphyxiation from deficiency of oxygen in water. (2) Air-breathing is not the only method of respiration in them, to the exclusion of water-breathing; but it rather supplements water-breathing to a more or less degree. The fishes experimented



upon are : *Amphipnous cuchia* ; *Mastacembelus pancalus*, *M. armatus*, *Rhynchobdella aculeata*, *Anguilla anguilla*, *Saccobranhus singio*, *Clarias magura*, *Anabas scandens*, *Trichogaster lalius*, *Ophiocephalus striatus*, *O. punctatus* and *O. gachua*. The two species of *Mastacembelus* and *Rhynchobdella aculeata* survived immersion for two to three days. Hence their aerial mode of respiration is an additional equipment for living out of water for some time.

### 39. On the branchial innervation of a few Teleostean fishes.

G. K. CHAKRAVARTY, Calcutta.

The investigation regarding the nerve supply in the gills of *Labeo rohita*, *Labeo calbasu*, *Cirrhina mrigala*, and *Catla catla* has revealed some difference from the mode of branchial innervation generally met with in Teleostean fishes. Instead of being supplied by the glossopharyngeal nerve only the first gill has its nerve supply partly by the glossopharyngeal and partly by the first branchial branch of the vagus. Unlike the general way where the second, third, and fourth gills are supplied by the first, second, and third branchial branches of the vagus respectively, the second, third, and fourth gills in these fishes have got some variation in the nerve supply. The second gill is supplied by the first and second branchial branches of the vagus, the third gill is supplied by the second and third branchial branches, and the fourth gill is supplied by the third branchial branch and another nerve emanating from the vagus. In addition to these nerves supplying the posterior region of the four gills, there are nerves which originate from the branchial branches of the vagus and supply the anterior region of the gills in different ways in different fishes.

### 40. The bionomics of a loach-like Siluroid fish *Amblyceps mangois* (Ham. Buch.).

S. L. HORA, Calcutta.

*Amblyceps mangois* is a long and slender fish that inhabits small streams at the base of hills in northern India, Burma, and Siam. The species varies considerably, especially with regard to the form of the caudal fin, the length of the adipose fin, the height of the body, etc., and has, consequently, been described under several names. A study of large material has shown that the genus, so far as known at present, is monotypic.

The author has observed this fish in its natural haunts in the Sevoke Stream in the Tista Valley below Darjeeling. It is a small stream with pebbly bed, and clear, rapid-running water. *Amblyceps* lives at the bottom where it can crawl with great agility and is able to seek shelter in holes and crevices among rocks and stones. An important factor in the habitat of the fish is the seasonal change in the volume of water in the stream. After a freshet the stream becomes a raging torrent, whereas during dry months it is cut up into a series of pools and puddles. *Amblyceps* possesses respiratory organs which are fully adapted to these changing conditions of existence. When living at the bottom of a torrential stream it respire like most of the hill-stream fishes, but during the hot and dry months, when the water dries up and the fish is forced to live in comparatively foul water, it resorts to aerial respiration. The behaviour of this fish is very similar to that of the funnel-mouthed tadpoles of *Megalophrys*, which live in similar situations.

### 41. The morphology of the skull of the Siluroid fishes.

B. S. BHIMACHAR, Bangalore.

This paper which embodies the results of an investigation of the osteological characteristics of the skull in the type forms of eight Indian



genera of Siluroids, deals primarily with the following features : There is a gradual ossification and specialization of the skull, more or less, in the following order—*Silundia*, *Plotosus*, *Wallago*, *Rita*, *Pangasius*, *Macrones*, *Arias*, and *Osteogeneosus*. The cranium slopes gradually before forwards. The skull is deeply situated in the primitive genera and becomes secondarily superficial in the higher forms. There is a well-developed orbitosphenoid, a suprasphenoid (fused with parasphenoid) and generally a toothed vomer. The cranium is platybasic and there is a thin cartilagenous internasal septum. The myodome is absent but a small trace of it is present in the primitive *Silundia*. There is generally a strong supraoccipital process. In the higher forms there is a rigid attachment with the cranium of the post-temporal and the complex vertebra the latter with secondary articulations also. The suborbitals and nasals are thin tubular bones. Two pterygoids are constant in all the forms. Palatines and maxillaries have undergone great modification. In two forms there are vestiges of the subopercula. The opisthotics and the parietals are absent.

#### 42. The skull of *Ophiocephalus striatus*.

B. S. BHIMACHAR, Bangalore.

The present paper is based on a comprehensive study of a large number of skulls of *Ophiocephalus striatus* and records among other features, the following most salient characteristics.

The bones on the dorsal surface of the cranium are large and are compactly articulated. There is no fontanelle. There is a small supraoccipital process and two epiotic lamellæ. The parasphenoid is long and possesses a small oval patch of teeth. Vomer is broad, toothed and extends in front of the supraethmoid. Orbitosphenoid is absent. There is a small suprasphenoid. The posterior myodome is closed behind. There is an anterior myodome on either side of the supraethmoid. The exoccipitals do not meet below the foramen magnum and each presents posteriorly an oval vertebral articular surface. The upper portion of the auditory region is compressed and on either side is a wide shallow recess below the parietal. This recess with an inwardly directed lamella of the hyomandibular forms the bony covering of the accessory air-breathing chamber. There are three pterygoids and a toothed palatine. The maxillary is edentulous. These points are discussed from a comparative standpoint of the allied groups.

#### 43. The relative condition of brain in fishes with reference to their habit and habitats.

B. K. CHATTERJEE, Calcutta.

(Communicated by Himadri K. Mookerjee.)

In studying the relative conditions of the brains in certain freshwater Teleostean fishes of Bengal, with reference to their habits and habitats, numerous variations as regards the structure, size, and weight of the brain were noticed.

#### 44. The golgi bodies in the erythrocytes of fishes.

D. R. BHATTACHARYA and S. P. BANERJI, Allahabad.

The occurrence of golgi bodies in the red blood-cells of reptiles and birds have been described by Bhattacharya and Brambell. This is the first time that they are being described in the erythrocytes of fishes. The authors examined a number of fishes and noticed the presence of golgi bodies as discrete elements in a diffused condition in the blood-cells of *Ophiocephalus punctatus* and several other fishes. The Da-Fano



slides proved to be less satisfactory than Ludford preparations. The golgi bodies lie mostly in a juxta-nuclear position and form a cap-like investment around the nucleus. They are granular in shape and are visible only with the aid of a high power oil immersion lens.

45. On certain peculiarities in the Vascular system of *Cacopus systoma* (Schneid).

M. S. MUTHUSWAMY IYER, Bangalore.

The following peculiarities are noticed in the Vascular system of this Engystomatid Toad :

1. Prolific branching of the Laryngeal artery into at least four principal branches.
2. The transverse Iliaco-communicans tends to shift anteriorly and opens into either the Reno-portal vein as in some or branches in the substance of the kidney.

A few other minor variations are also described.

46. On the Tympanic Membrane of certain Engystomatidæ.

L. S. RAMASWAMI, Bangalore.

The tympanic membrane described in text-books such as Ecker's Frog is fibrous and is stretched and held in position by the cartilaginous Annulus Tympanicus. The skin covering the membrane is thinned out. In *Bufo* the tympanic membrane is no doubt as in *Rana* and the skin covering the membrane has lost the glands though the small tubercles are present. In *Cacopus* the tympanic membrane has become cartilaginous and is situated at the angle of the mouth. This tympanic membrane is unattached to the overlying skin, which histologically is exactly like the skin in the other parts of the body. The attachment of the columella to this cartilaginous tympanum and the structure of the middle and the internal ear form the subject matter of the paper.

This extraordinary modification of the tympanic membrane is in accordance with the singular life habits of the animal.

47. The heart of *Ureotyphlus menoni*.

K. KARUNAKARAN NAIR and A. SUBBA RAU, Bangalore.

The description of the structure of the heart of this amphibian is given.

48. On the arterial arches of *Ureotyphlus menoni*.

H. K. MOOKERJEE and B. K. CHATTERJEE, Calcutta.

In the vascular system of *Ureotyphlus menoni* certain peculiarities in the disposition of the arterial arches were observed. From the long and stout truncus arteriosus, arise the four trunks simultaneously, (1) two systemic, and (2) two pulmonary. The two pulmonary trunks run only a short distance with the systemics, and then, relative to the inequality and asymmetry of the lungs, they are unequal in size and asymmetrical in disposition. The systemic trunks are long and extend up to the base of the skull where they arch back and unite with each other behind the apex of the heart, to form the Dorsal Aorta. The carotids arise from the systemics at the points where they bend down. The ductus botalli are distinct elongated vessels running along the systemic trunks.



49. Notes on the peculiar apertures in the vertebral-centra of *Typhlops braminus*.

H. K. MOOKERJEE and G. M. DAS, Calcutta.

It has been observed from an alizarine preparation of transparency of *Typhlops braminus* that each vertebra has an aperture in the middle of the ventral surface of the centrum towards the anterior half. These apertures are present throughout the vertebral column up to the pelvic region beyond which in the tail vertebræ they are absent.

50. On the urinogenital organs of common Indian lizard—*Calotes Versicolor*.

J. DAYAL, Lucknow.

Very little is known about the urinogenital organs of the common Indian lizards. The kidneys lie at the posterior end of the abdominal cavity and the ureters open into a dorsal pouch of cloaca (Urodæum). The testes are paired organ lying far forwards in the abdominal cavity by the side of the vertebral column. The Vasa-defferentia open separately into the urinary chamber. Copulatory organs are present in the males. The ovaries also lie in the middle of the abdominal cavity. The oviducts open anteriorly into the abdominal cavity and posteriorly into the cloaca.

A detailed account of the urinogenital organs is given. The paper concludes with a comparison of its urinogenital organs with those of *Hemidactylus* and *Uromastix*.

51. On the so-called three species of *Cylindrophis* Wagler.

B. C. MAHENDRA, Agra.

The author has made a careful examination of a fairly representative collection of snakes belonging to the genus *Cylindrophis* Wagler, and he finds that the so-called 'specific' features between *Cylindrophis maculatus* Linné, *C. rufus* Laurenti, and *C. lineatus* Blanford do not really serve to mark off one 'species' from the other. All these features grade indiscriminately, and there is actually no discontinuity, which can be regarded as sufficient ground for instituting three species. He suggests that the three forms be regarded as colour varieties of the same species *C. maculatus* Linné.

It is also shown that the colour pattern in *C. rufus* is a modification of the one found in *C. maculatus*. In the latter, the black network enclosing two series of spots along the back is formed by three longitudinal stripes visible from above and a number of alternating cross-bands. In the former, the arrangement is the same, but the longitudinal stripes are absent, thus leaving a number of half cross-bands on the body, alternating with each other.

52. The yolk nucleus of Balbiani in the Oogenesis of *Columba intermedia*.

R. S. DAS, Allahabad.

In Da Fane's silver nitrate preparation and also in Mann Koosch as modified by Ludford it has been observed that the initial focus of growth of golgi bodies and mitochondria is restricted to the centrosphere area juxtannuclear in position. This area is also seen in the preparation of histological fixatives carrying centrosome with a centriole. In young oocytes, this archoplasmic area seems to be the seat of the greatest activity in the cell. The cytoplasm in this area is of much denser consistency and in their earlier stages golgi bodies and mitochondria are restricted



to this area only. In other words this area or as D'Hollander calls it 'Yolk nucleus of Balbiani' is the seat of important vital functions in the life of an oocyte.

53. On a cyclopic chick monster.

M. B. LAL, Lucknow.

This chick monster collected locally shows four developing wings and four posterior limbs. Head and other parts are normal. Details of the Monstrosities are discussed in the paper.

54. The skeletal system of a microchiropteran, *Rhinopoma microphyllum*.

H. K. MOOKERJEE, Calcutta.

The salient features of the skeletal system are as follows :—

1. Neural spine in fourth, seventh, and eighth thoracic vertebræ.
2. Ilium is articulated with the two vertebræ.
3. Ischium is articulated with another two vertebræ.
4. Pelvic girdle :—
  - (a) Epipubic bone or so-called Marsupial bone which is diagnostic feature of the group marsupialia has not hitherto been recorded in other mammalia except, of course, in the monotremata.
  - (b) Ischia having a symphysis in front.

55. The eyes of *Loris Lydekkerianus*.

A. SUBBA RAU, P. R. SUBBA RAO, and S. HIRIYANNAIYA, Mysore.

The eyes were examined with the aid of the Ophthalmoscope and the slit lamp. The arrangement of the blood vessels and the general appearance of the fundus are described. The band pattern as revealed by slit lamp examination of the eye of this interesting Primate is recorded. A brief description of the structure of the retina is offered.

56. Notes on congenital abnormality of the limbs of man.

S. HIRIYANNAIYA and K. SUNDARESAN, Mysore.

(Communicated by Prof. R. G. Aiyar.)

Congenital absence of the Radius and Ulna in the upper limb and of the Fibula in the lower limb of a man is noted. The X-ray appearance of the knee-joint is given. The factors causing deformities of the limbs are discussed.

57. Cytoplasmic inclusions in the oogenesis of *Sciurus palmarum*.

MISS R. CLEMENT, Allahabad.

The oogenesis of the squirrel has been worked out by fixed preparations as well as by intra vitam and vital staining experiments. The golgi bodies appear in a juxta-nuclear position in young oocytes both in fixed and fresh preparations.

The golgi bodies in very early stages appear to form a network. Later on they present a vesicular or crescentic form having a duplex structure, an outer osmiophilic rim and a central chromophobic portion. In advanced stages of oogenesis, the golgi bodies form a peripheral ring



and yolk formation takes place at this stage by the swelling up of the golgi elements. The infiltration of golgi elements from the follicular epithelium to the egg can easily be demonstrated. Mitochondria appear in patches in fixed preparations. In early stages they are concentrated like golgi bodies in the 'Yolk nucleus of Balbiani' area. With the growth of the oocyte they are evenly distributed in the Cytoplasm, and do not appear to take part in Vitellogenesis. Distinct nucleolar extrusions are present but take no part in Vitellogenesis. By vital staining experiments particularly with neutral red the vacuome can be demonstrated. It is distinct from golgi bodies which remain unaffected by this dye. The yolk bodies are stained by Sudan III and Scharlach R. A number of vacuoles are present, in some cases having their interior filled with some sort of Coagulum. In the squirrel the yolk seems to be fatty in nature.

58. The ovary and the ovarian ovum of *Pteropus medius*,  
Dobs.

B. R. SESHACHAR and L. S. RAMASWAMI, Bangalore.

The paper records certain extremely interesting observations on the structure of the ovary and the ovarian ovum of *Pteropus* in different stages of growth and development. A careful examination of a large series of the sections of the ovary of this interesting bat points to the conclusion that there is a polar aggregation of younger ova while the fully formed ones are found at the opposite pole. The cytoplasmic inclusions like the mitochondria and the golgi bodies are periodic in their occurrence and are confined to certain stages in the developmental phenomena. Definite information is available as regards the rôle played by these inclusions in the elaboration of fat and vitellogenuous products. So far as the developmental phenomena of the oocytes are concerned *Pteropus* perhaps differs from the other members of the Chiroptera.





# INDIAN SCIENCE CONGRESS.

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Twentieth Annual Meeting,  
PATNA, 1933.

## ABSTRACTS OF PAPERS.

### Section of Geology.

*President :—Prof. N. P. Gandhi, M.A., B.Sc.,  
A.R.S.M., A.I.M.M., F.G.S., D.I.C.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET,







## Section of Geology.

### *Abstracts.*

#### MINERALOGY.

1. Felspars in the amygdales of the Lingadhalli traps.

CHARLES S. PICHAMUTHU, Bangalore.

In a previous communication to this section of the Congress, the author came to the conclusion that the spots and patches found in the trap rocks of Lingadhalli are metamorphosed amygdales. A detailed examination of the mineral contents of these amygdales has now revealed the presence of a colourless mineral with a radiating habit and exhibiting multiple twinning. Staining tests, specific gravity, and refractive index measurements, and a study of its optical characters by means of the Fedorov Universal Stage have resulted in the identification of the mineral as a plagioclase of composition  $Ab_{65}An_{35}$  (andeclase).

2. On the occurrence and distribution of staurolite in Gangpur State, Bihar and Orissa.

M. S. KRISHNAN, Calcutta.

Staurolite occurs in mica-schists (1) in a zone parallel to and adjoining a large epidiorite sill extending from Gailo ( $22^{\circ} 4' : 84^{\circ} 44'$ ) to Rabga ( $22^{\circ} 4' : 84^{\circ} 29'$ ), (2) along the borders of some granite bosses, and (3) apparently unconnected with intrusives, as along the centre and borders of the Gangpur anticlinorium. The crystals show the development of  $m$  (110),  $b$  (010),  $c$  (001) and  $r$  (101); *plus*-shaped twins on (032) where the individuals cross at right angles, X-shaped twins on (232) crossing at nearly  $60^{\circ}$ , and six-rayed trillings also twinned on the pyramidal face.

The rocks of the area show clear evidences of regressive metamorphism from the *meso* to the *epi* grade. The regional metamorphism to which the area was subjected seems to have been sufficient for the formation of staurolite, but the intrusive rocks have helped to perfect the conditions by raising the temperature and increasing the molecular mobility in their neighbourhood.

3. Microscopic characteristics of the copper ores of Singhbhum.

M. C. PODDAR and S. K. ROY, Dhanbad.

#### PETROLOGY (IGNEOUS).

4. On the occurrence of an uralitic gabbro near Vajrat, Sawantwadi State.

K. V. KELKAR and R. D. GODBOLE, Poona.

The rocks forming the hills to the south of Vajrat, about six miles north-east of Vengurla, were found to vary between a gabbro and an uralitic gabbro containing plagioclase and uralite. In thin sections the gabbro exhibits plagioclase, augite (in part diallagic), and a little



orthorhombic pyroxene. The accessories are magnetite and biotite. The augite has slightly altered to secondary amphibole at the margins. Confused aggregates of magnetite grains and colourless secondary amphibole, showing a ring of green amphibole where in contact with plagioclase, have probably resulted from original olivine. Pink garnet also occurs as a corona mineral, either alone or with green amphibole. Commonly the rocks are dark and have a medium-grained granitic texture. The rock is intrusive in an Archæan granite-gneiss and some quartzites of uncertain age.

5. A note on some basic intrusions in South Belgaum District.

W. K. PATWARDHAN, Poona.

The paper contains a description of several dolerites intruding the granite-gneiss and Dharwars in South Belgaum District. They are dark coloured and have a fine to medium-grained texture. Two types are common: some contain augite, plagioclase, a little biotite and magnetite, the quartz forming micrographic intergrowth with plagioclase; other equally common types contain magnetite and biotite as accessories, and olivine, enstatite, augite and plagioclase. A single compact basaltic rock was found. It contains phenocrysts of augite, enstatite and decomposed olivine. In the groundmass are commonly seen untwinned plagioclase needles forming fan-like groups, and augite, biotite, and magnetite.

6. On the petrography of the porphyry dykes near Mandya—I.

S. RAMACHANDRA RAO and CHARLES S. PICHAMUTHU,  
Bangalore.

The paper is a petrographic study of two types of porphyritic dyke rocks occurring about 6 miles to the south of Mandya. One of the dykes is a monzonite porphyry containing phenocrysts of orthoclase, plagioclase, and hornblende. The orthoclases, which are flesh-coloured, occur in very well-formed crystals, many of which are found loose in the weathered portions of the dyke. The groundmass is composed of a panidiomorphic aggregate of plagioclase. The specific gravity is about 2.61. The other dyke contains porphyritic crystals of plagioclase, hornblende, and biotite set in a fine-grained felspathic matrix. Many of the phenocrysts of plagioclase show well-defined zoning; quartz occurs sparingly in irregular grains. The specific gravity is about 2.68 and the rock may be described as a tonalite porphyry.

7. Notes on the mica-bearing pegmatites of Nellore.

S. L. BISWAS, Calcutta.

In Nellore the mica-pegmatites cut through biotite-schist which shows a very high concentration of biotite at the contact zone. In some cases the minerals of the biotite-schist disseminate into the pegmatite vein and xenoliths of this country rock may also be noticed in the vein near the margin. All these clearly indicate the effect of the pegmatitic intrusions at the contact zone. In many veins there are numerous inclusions of muscovite-schist, ranging in size from one inch to one yard across, indicating remnants of inclusions caught up by the vein in the deeper region. This appears to corroborate the author's view that the genesis of muscovite in the productive veins may be attributed to assimilation of muscovite-schist in the deeper regions.



8. On the corundum-bearing rocks in the Namakkal Taluk, Salem District, Madras Presidency.

L. A. NARAYANA IYER, Calcutta.

The rocks referred to in this paper are found south of Sittampundty. Mr. C. S. Middlemiss has published a note on these corundum rocks in *Rec. Geol. Surv. Ind.*, XXIX. The present paper deals with the suite of rocks associated with them.

The corundum rock is a pale grey or white anorthite-gneiss, with varying amounts of hornblende and with accessories as garnet and some chondrodite. The corundum is surrounded by a lighter coloured shell of felspar. The anorthite-gneiss is accompanied by a series of intrusives varying from ultrabasic, basic and acid. These different intrusions suggest that there has been a differentiation and fractionation of a basic magma in this area, which has given rise to the large exposures of anorthite-gneiss, in which the other members are intrusive.

The ultrabasic fraction is represented by a chromite-pyroxene rock, the basic by a garnet-pyroxene-plagioclase-rock with synantetic intergrowths round the garnets, and the acid by pegmatite dykes and quartz veins. The evidence obtained from this suite of rocks suggests that there was an oversaturation in the anorthite portion of the magma with alumina, which subsequently crystallised out as corundum.

**PETROLOGY (SEDIMENTARY).**

9. The graphical representation of heavy mineral analyses.  
P. EVANS, R. J. HAYMAN, and M. A. MAJEED, Digboi, Assam.

The accessory minerals of arenaceous rocks have received much attention in recent years as it has been found that valuable aids to correlation can sometimes be obtained by a comparison of the minerals from different areas. Attention is usually concentrated on the heavy residues obtained by separation with bromoform but there is no general agreement either as to the manner in which the analyses of the minerals should be carried out or as to the manner in which the results should be represented.

The relative abundance of different minerals may be obtained either by rough estimation or by careful counting and may be indicated by symbols, by an arbitrary scale from 1 to 9 or 10, or by percentages. Except in very simple cases, it is almost impossible to tabulate the results in such a way as to bring out clearly the differences between the mineral suites of different localities and horizons. The successful application of the micropetrological method depends largely upon the readiness with which the available data can be compared and graphical methods have a very great advantage over tabulation. The geologists of the Burmah Oil Company have worked out a graphical method of representation of accessory mineral analyses which has been of great use in Assam. The stratigraphical position of each sample from any particular section or locality is plotted horizontally on squared paper and the mineral frequencies are plotted vertically using a special scale which is nearly logarithmic (i.e. geometrical progression). The paper includes three examples of such 'range tables'.

10. The graphical representation of mechanical analyses of sands.

P. EVANS, W. B. METRE, and B. H. SINGH, Badarpurghat, Assam.

The detailed examination of a sediment includes the estimation of the proportions of grains of various sizes, which (for sands) is most



conveniently done by the use of sieves. The technique of such mechanical analysis is very simple, but the representation of the results often fails to bring out clearly the differences and resemblances between a number of samples.

There are two usual methods, the cumulative percentage curve and the histogram. In the former, the grade size is plotted horizontally, usually on a logarithmic scale, and the cumulative percentages by weight of the various grades are plotted vertically, so that each curve runs from 0 on the left to 100 on the right, differing in slope according to the composition of the sample. The drawback is that the distribution of grains between different grades is not sufficiently clearly shown. The histogram consists of a series of rectangles with lengths proportionate to the percentages of grains within definite grades—usually not of equal range but in geometric progression. The drawback is that only one sample can conveniently be shown on one figure and the varying range of diameters may make comparison difficult.

The method used by the writers overcomes these objections. From the cumulative percentage curve plotted on ordinary (not logarithmic) paper the first differential is obtained graphically by subtracting successive points on the cumulative curve for intervals of, say, 0.05 mm. This gives a curve showing the percentage of each 1/20 mm. grade of sand. Several curves can be drawn on one sheet and comparison is greatly facilitated. The paper includes several examples of these curves.

# 11. The heavy minerals in the Barakar and Raniganj Series of the Jharia Coalfield, Bihar.

M. C. PODDAR, Comilla.

*(Communicated by P. Evans.)*

The heavy mineral residues of over a hundred samples of sandstones in the Barakar and Raniganj Series of the Jharia Coalfield have been separated by bromoform and analysed.

The assemblage found in the Barakar Series consists mainly of magnetite, ilmenite, zircon, rutile and tourmaline. The Raniganj assemblage consists mainly of garnet with much smaller amounts of magnetite, tourmaline and zircon and very little rutile. There is thus a clearly marked difference between the two mineral suites, enabling the series to be distinguished.

From the analyses and stratigraphical position, range-tables have been drawn out on the lines devised by the Burmah Oil Company's geological staff. Although the sampling was not carried out at very close intervals, the range-tables for six different sections show a fair measure of correspondence. The Barakar Series can be subdivided into four unequal stages on the basis of the variations in tourmaline and zircon; these are not very striking but are probably recognisable throughout the Jharia field. It is not improbable that with more detailed work, micropetrological evidence would be of assistance in correlating the different seams.

## PETROLOGY (METAMORPHIC).

# 12. The origin of the streaky gneisses of the Nagpur district.

W. D. WEST, Calcutta.

Associated with the metamorphic rocks of the Nagpur district known as the Sausar series, there occur large areas of coarsely banded 'streaky gneisses' which, treated as a whole, bear a discordant relation towards the Sausar series. From certain favourable exposures on sheet 55<sup>g</sup>, which show these gneisses in the early stages of formation, evidence is



adduced to show that they have in the main been formed by the intimate penetration of a biotite-granulite of igneous origin by veins of aplite on an immense scale. In some cases the para-schists of the Sausar series have likewise been penetrated to give streaky gneisses difficult to distinguish from those of wholly igneous origin.

It is concluded that there was first an intrusion of large masses of granodioritic magma, followed soon after by the intrusion of a more acid aplitic magma, which penetrated both the granodiorite (now a biotite-granulite) and the schists of the Sausar series in a very intimate manner, giving rise to banded gneisses of composite origin.

### 13. On some Dharwarian conglomerates from Chota Nagpur and Jubbulpore.

M. S. KRISHNAN, Calcutta.

There are several occurrences of crush-conglomerate in Gangpur State, Bihar and Orissa, and in the neighbourhood of Sleemanabad ( $23^{\circ} 38' : 80^{\circ} 15'$ ) in the Jubbulpore district, C. P. In the Gangpur area the conglomerates include gritty, crushed, and sheared types, containing pebbles of quartz, quartzite, biotite-schist, tourmaline-quartz-rock, and rarely granite. In the Jubbulpore area the pebbles are of quartzite, cherty quartz, and banded hæmatite-quartzite. The matrix generally contains quartz, mica, sericite, chlorite, and magnetite.

In some cases the pebbles are large and well-rounded and in others sub-angular and distinctly crushed. All gradations from rocks which may be considered to be clearly sedimentary to those which may be called autoclastic are met with. The author is of opinion that practically all the conglomerates studied were originally of sedimentary origin, but crushed and sheared later, though locally true autoclastic conglomerates might have been produced.

## STRATIGRAPHY (OLDER ROCKS).

### 14. A preliminary account of the metamorphic rocks of the Darjeeling area.

SANTOSHKUMAR RAY, Calcutta.

In 1902 Mr. J. Parkinson described the petrography of the Darjeeling series of Mr. Mallet, and established the presence in it of a garnetiferous sillimanite-gneiss and an 'eye' rock, viz. a quartz-garnet-pyroxene rock. In the present paper, which includes a description of a wider area, a few additional types of rocks of the Darjeeling series have been described, viz. a garnetiferous kyanite-gneiss, a felspathic mica-schist with tourmaline and staurolite-bearing varieties, and a quartz-felspar-garnet-sillimanite rock. This paper also includes the description of a tourmaline-bearing phyllite and a garnetiferous phyllite, which form part of the Daling series of Mr. Mallet. The presence of staurolite in some of the rocks has been noted here for the first time. Representatives of the gneisses, schists, and the phyllites have been analysed chemically. The agreement in chemical nature between the gneiss and the schist has been pointed out, and a para-metamorphic origin has provisionally been ascribed to the rocks from a study of their chemical, mineralogical, and field characters.

### 15. Notes on the geology of Vengurla Peta.

K. V. KELKAR and P. K. LOHOGAONKAR, Poona.

The commonest rock of the Archæans is a gneissose granite with prominent felspar (chiefly orthoclase) phenocrysts. The constituents



are orthoclase, microcline, quartz, biotite, plagioclase, myrmekite, apatite, etc. A few hornblende and biotite-schists, occasionally garnetiferous, are noticed with epidiorites, muscovite-gneisses and quartz veins striking E. by N. to W. by S., with a steep dip to N. by W. With these is associated a series of almost vertical beds with foliated conglomerates and breccias with lenticles of quartz, including red banded jasper, quartzites and much weathered pyritised hornblende-schists, epidiorites, etc. striking N. by W. from Nivti and running up to Malwan. Unlike the Kaldagis these are highly disturbed, show cataclastic structures and contain metamorphosed basic rocks and hence are referred by the authors to the Dharwars. Other formations met with in the area are a dyke of Deccan Trap, Konkan laterite, recent shore sands, etc.

16. Geology of the country around the Indian School of Mines, Dhanbad.

O. L. DADHEECH and S. K. ROY, Dhanbad.

**STRATIGRAPHY AND PALÆONTOLOGY (ARYAN).**

17. A note on the Cullygoody limestone.

L. RAMA RAO and C. PRASANNAKUMAR, Bangalore.

The Cullygoody limestone, so called because of its abundant occurrence north and south of the village of Cullygoody, forms one of the most important bands of coral limestone associated with the Trichinopoly Cretaceous. A brief descriptive account of this rock is given by Blanford (*Mem. Geol. Surv. Ind.*, IV). He has also discussed at some length the age of this limestone and has adduced several arguments in support of its being considered as of the same age as the coral limestone at the base of the Utatur beds. The Cullygoody limestone has now been studied by the authors, both in the field and in the laboratory. Though the rock may generally be described as a coral limestone, the study of a large number of micro-sections has revealed the additional occurrence of numerous interesting types of Microzoa—chiefly foraminifera and radiolaria. But by far the most important feature of the fossils in this limestone is the occurrence of numerous algæ, particularly in one type of this limestone. Considering that this bed is of Utatur (Cenomanian) age, it is obvious that this occurrence of Cretaceous algæ in India is even older than that in the Niniyur rocks.

18. On the flints and cherts of the Niniyur stage.—III.

L. RAMA RAO and C. PRASANNAKUMAR, Bangalore.

The paper deals with an intensive study of the several bands of flints and cherts round about the village of Vilangudi, a brief reference to which has been made by Blanford in his Memoir on the Trichinopoly Cretaceous. A large number of representative specimens has been collected and studied both in hand specimens and in micro-sections. It has thus been possible to distinguish several types of these flints and cherts, on micro-structural and palæontological considerations. A point of great interest and importance is the occurrence of numerous algæ—chiefly *lithothamnion*—in many of these types. The important question of the exact age and mode of origin of these flints and cherts is briefly discussed, in the light of the new evidences now available.



## 19. On the age of the Quilon bed.

A. K. DEY, Calcutta.

The Quilon limestone bed known through the researches of General W. Cullen is exposed at a place called Padappakara, 7 miles N.E. of Quilon, Travancore. During the field season 1926-27, the writer made a rich collection of fossils from Padappakara. The fossils consist of foraminifera, corals, echinoids and molluscs. Of these the representatives of the last-named are most abundant. The fauna shows affinities with those of the Gaj and Karikal beds of India, while several species are identical with those of the Miocene and Pliocene beds of the Dutch East Indies. The study of the molluscs shows that the Quilon bed fauna, in spite of its distinct admixture of Pliocene types, has essentially a Miocene character. The absence of any typical Oligocene species, and the presence of several Karikal forms, suggest the upper limit of the Gaj or Burdigalian to be the probable age of the Quilon bed.

## 20. Gasteropods from the Quilon limestone.

CHARLES S. PICHAMUTHU and C. PRASANNAKUMAR, Bangalore.

In a previous communication to this section of the Congress, the authors reported the re-discovery of the Quilon limestone *in situ* and also described a few fossils collected from the area. The present paper embodies a description of a number of gasteropods from these limestones, which form the majority of the fossils. Their identification further confirms the view that the Quilon limestone represents a mixture of the Burmese and Sind facies.

## COAL.

## 21. Action of certain solvents on Indian coal.

N. N. CHATTERJEE, Calcutta.

The present paper embodies the results of the study of the action of pyridine and chloroform on some of the Gondwana coals. The specimens include (i) Giridih coal obtained from Ramnadih Colliery, Giridih, (ii) Dishergarh coal from Aldih Colliery, Raniganj coalfield, (iii) Poniat coal from S.E. Baraboni Colliery, Raniganj coalfield, (iv) Ratibaty coal from Ratibaty Colliery, Raniganj coalfield, and (v) Ghusick coal from Ghusick Colliery, Raniganj coalfield. The alpha, beta, and gamma compounds have been determined quantitatively and their relationships with the caking and swelling properties have been discussed.

## 22. A short note on some Indian fusains.

N. N. CHATTERJEE, Calcutta.

In the paper the author has described the results of the physical and chemical study of fusains collected from several coal-seams of different geological ages. The specimens under discussion were obtained from (i) Talchir coal, Villier's Talchir Colliery, Orissa (Talchir stage), (ii) No. 14 seam coal, Ekra Colliery, Jharia coalfield (Barakar stage), (iii) Jilbari coal, Rajmahal hills (Barakar stage), (iv) Bora Dhemo seam, Lachipur Colliery, Raniganj coalfield (Raniganj stage), and (v) from Ara coal, Bhaganwallah coalfield, Salt Range (Laki stage, Lower Eocene). The results of a detailed chemical study in the shape of proximate and ultimate analyses of the specimens have been given in the paper. After the treatment of maceration by the Schulze solution for several days the fusain specimens were studied under the microscope, which revealed the presence of several rows of well-preserved bordered pits of different shapes in all except the Salt Range specimen.



## 23. Studies in the coal problem by x-ray diffraction methods.

C. MAHADEVAN, Lingsugur.

A brief description of the technique for the study of the coal-problem by x-ray diffraction methods is given. The fundamental difference, as revealed by x-ray studies, in the nature of vitrain, durain and fusain is brought out. Vitrain patterns are due to particles of colloidal dimensions; the durain pattern is found to be made up by superposing 'ash' and graphitic carbon spacings on the vitrain pattern. Fusain gives halos ascribable to ash and free carbon; localised spots of intensity indicate the persistence of fibre-structure. From a study of the x-ray scattering index in relation to the 'proximate analysis', a correspondence of the scattering index and the sum of 'moisture content' and 'volatile matter' rather than of either of them individually, is observed. This points to a close association of these ingredients. Of the products of breaking up coals into their so-called alpha, beta, and gamma compounds, the alpha and beta compounds are seen to give patterns nearly identical. The gamma compound pattern is quite distinct and shows similarity of structure to the x-ray pattern for resins. The x-ray patterns for the tertiary coals are seen to differ slightly but distinctly from those for the permo-carboniferous coals in spite of very similar 'proximate analyses'. The significance of this result is discussed in detail.





# INDIAN SCIENCE CONGRESS.

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## ABSTRACTS OF PAPERS.

### Section of Chemistry.

*President :—Dr. H. B. Dunnicliff, M.A., Sc.D., F.I.C.,  
I.E.S.*

CALCUTTA.

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## Section of Chemistry.

### *Abstracts.*

#### 1. The electro-chemical restoration of bronze images.

S. PARAMASIVAN, Madras.

Dr. A. Scott of the British Museum criticises the electro-chemical process of Restoring Bronze images and holds that (1) when a completely mineralised image is subjected to electrolytic treatment, it is reduced to a fine powder and it crumbles away; (2) under this process, there is always a plating of copper on the image; (3) this coating of copper encloses chlorine-containing compounds; (4) considerable knowledge of electro-chemical methods is needed and that the method is too complicated and not safe for use in ordinary museums.

Investigations were carried out to test these conclusions. No plating phenomenon is observed and there is complete absence of chlorine-containing compounds over the image at the completion of the electrolytic restoration.

In restoring completely mineralized specimens (where the object is to reduce the outer crust), all the chemical methods are defective, and the electrolytic method is safer. Though the method is complicated the results are more uniform than under the chemical methods.

#### 2. The influence of (a) charcoal, and (b) sulphur on the decomposition of ammonium nitrate.

M. S. SHAH, Ahmedabad.

The decomposition usually starts in presence of charcoal at about  $169^{\circ}5$ , the melting point of ammonium nitrate. Much heat is liberated and the reaction soon becomes violent. The reaction products are: (nitrous oxide, water vapour) carbon dioxide, nitrogen, nitric oxide, nitrogen peroxide, and nitric acid. The latter accumulates in the initial stages of the process and is reduced by charcoal at the end of the reaction evolving much nitrogen peroxide.

Sulphur does not affect the decomposition appreciably below  $240^{\circ}\text{C}$ . Above that temperature the reaction is slightly accelerated and some sulphur trioxide is formed. Sulphur dioxide is evolved only in traces when all the ammonium nitrate has practically decomposed.

#### 3. The interaction between Zinc and aqueous solutions of ammonium nitrate.

M. S. SHAH and S. S. DESAI, Ahmedabad.

A dry mixture of zinc dust and ammonium nitrate ignites when treated with a little water. The reaction has been studied quantitatively with (a) varying amounts of zinc dust, and (b) varying concentrations of ammonium nitrate solution. The heat of reaction has been measured accurately in each case.

#### 4. Removal of Titanium from impure specimens of Niobium.

S. G. KIRI and K. R. KRISHNASWAMI, Bangalore.

Existing methods for the separation of mixtures of niobium and titanium are tedious and difficult to carry out.



The method described consists in converting the mixed oxides into their respective potassium complex oxalates and fractionally recrystallizing them. Satisfactory results have been obtained.

The difficulties of the colorimetric hydrogen peroxide method for estimation of small quantities of titanium in presence of niobium and the spectrographic method employed for the purpose are fully described.

5. The properties of Cobaltous Oxide prepared at different temperatures.

T. S. SURATKAR, S. M. MEHTA, *and* MATA PRASAD, Bombay.

One of the authors had previously studied the properties of nickelous oxide prepared at different temperatures and had shown the importance of these results in the separation of nickel from nickel-copper matte.

The present investigation contains the results of a similar study of the properties of cobaltous oxide prepared at different temperatures. It has been found that fairly pure sample is obtained by heating cobalt carbonate above 900°C. The oxide contains active oxygen the amount of which decreases as the temperature of preparation is raised. Also with an increase in the temperature of preparation of the oxide, the colour of the oxide changes from yellow to brown, and its density and electric resistance increase while the catalytic activity in the decomposition of  $H_2O_2$  and the solubilities in sulphuric and hydrochloric acids decrease. The decrease in solubility in sulphuric acid is not so remarkable in the case of cobalt oxide as in the oxide of nickel.

6. The compounds of Dimethylglyoxime with Cobalt Chloride.

P. R. RAY, Calcutta.

Feigl and Rubinstein (*Annalen*, 1923, **433**, 186) have described the preparation of a green compound in acetone solution from cobaltous chloride and dimethylglyoxime. The exceptional stability of the compound, which does not react with any characteristic reagent for cobalt or dimethylglyoxime, led them to assume that it represents a case of strong cobaltous complex with a co-ordination number four. The chlorine atoms lying outside the complex zone were found to act readily with silver nitrate. They also observed that the substance in aqueous solution gives an acid reaction owing to hydrolysis. From a study of the magnetic susceptibility and other physical and chemical properties of the compound, it is now shown that the substance is really a cobaltic complex, and not cobaltous, as suggested by Feigl, Paneth, Thilo, Dübsky, and Brychta. Some new derivatives of the compound have also been prepared and studied.

7. Preparation of Thorium and Cerium Nitrates from indian Monazite sand.

M. S. PATEL *and* S. G. DEO, Bombay.

Fractional precipitation methods for the preparation of thorium from other rare earths has been tried with ammonium hydroxide and sodium carbonate. Digestion of the rare earth oxalates with ammonium acetate has been tried. Digestion of sand with different volumes of concentrated sulphuric acid for varying periods is being tried to find out optimum condition of complete digestion.



### 8. Preparation of Alumina and Aluminium Sulphate from indian Bauxite.

M. S. PATEL, G. E. OGALE, and P. V. PARANJPE, Bombay.

Samples of Bauxite from various localities have been analysed. The solubilities of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2$  in acids have been determined. Heating of bauxite at  $110^\circ$  prior to acid treatment has been found to affect the solubility of the above components. All the samples contain silica. In some of the samples of bauxite, silica is in chemical combination. Fusion with sodium carbonate gives better results than digestion with caustic soda. The effects of moisture and presence of organic matter in the mineral have also been studied. Action of sulphur dioxide in presence of water under different conditions is being studied.

### 9. Sodium Carbonate and Bicarbonate from efflorescent natural soda.

M. S. PATEL and P. S. RAO, Bombay.

Samples of natural soda from various localities in the Bombay Presidency have been analysed. The study of the systems  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  at  $29^\circ$ ,  $33^\circ$ ,  $40^\circ$ ,  $60^\circ$ ,  $65^\circ$ , and  $80^\circ\text{C}$ . is being carried out with useful results.

Simplification of the above systems by converting  $\text{NaHCO}_3$  into  $\text{Na}_2\text{CO}_3$  by passing steam into the mixture has been tried. A study of the natural process as it takes place in the soda fields has also been made. The results so far obtained show that under proper conditions of temperature and concentration it will be possible to obtain fairly pure sodium carbonate for industrial purposes from efflorescent natural soda.

### 10. The action of Hydrogen Sulphide on Chromates

#### Part III Potassium Dichromate.

H. B. DUNNICLIFF, Lahore.

In the intermediate stage, a brown precipitate containing  $(\text{CrO}_2)_x$  is formed. Thiosulphate is first developed in the precipitate and this passes into the alkaline liquid phase. Sulphide is absent from the liquid so long as any chromate ion is present. So long as any hydrogen ions are present, some tetrathionate is formed by the oxidation of thiosulphate but none is formed when the solution is alkaline. This tetrathionate is ultimately converted into thiosulphate and sulphur by the action of potassium sulphide. Thus the final products are (a) a precipitate containing chromium hydroxide, co-ordinated chromium thiosulphate in which the ratio of ionic to co-ordinated ( $\text{S}_2\text{O}_3$ ) is 2 : 1 and sulphur, and (b) potassium polysulphide ( $\text{K}_2\text{S}_3$ ) and thiosulphate in solution. Sulphate is absent.

### 11. The action of Hydrogen Sulphide on Potassium ortho- and metarsenites.

H. B. DUNNICLIFF, Lahore.

An apparatus is described in which an attempt is made to determine the exact composition of the sulphide of arsenic,  $\text{As}_2\text{S}_3$ ,  $x\text{H}_2\text{S}$  which separates from strong solutions.



## 12. Complex Oxalates of Niobium, Tantalum, and Titanium.

D. S. N. MURTHI, S. G. KIRI, and K. R. KRISHNASWAMI, Bangalore.

Russ (*Z. anorg. Chem.*, 1902, **32**, 42) prepared potassium niobium oxalate and assigned to it the formula  $3\text{K}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 6\text{C}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ . The authors have repeated the work under modified conditions and obtained the same compound as well as another stable hydrate.

They have not been able to obtain potassium tantalum oxalate having a definite composition as the preparations contained varying proportions of oxalic acid.

Potassium titanium oxalate about which there is no mention in literature has been prepared in a pure state and found to have the composition corresponding to the formula  $\text{K}_2\text{O} \cdot \text{TiO}_2 \cdot 2\text{C}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .

The solubility and the conductivity of the titanium as well as the niobium salt have been determined and are discussed in the paper.

## 13. Decomposition of Sulphur Dioxide in electric discharge due to alternating fields of low frequency.

S. S. JOSHI and K. K. SHARMA, Benares.

The apparatus resembled the familiar Siemens Ozoniser. Even though the ionisation space was about 3 mm. wide, the decomposition was sensible with such low pressures as less than 10 cm. Hg by voltages of the order of 10,000. The progress of the decomposition is represented by pressure-time curves. It has been found that the rate of the change at a constant applied potential diminishes as the gas pressure is increased and that it increases by increasing the applied potential with constant gas pressure. The final mixture consists of unchanged  $\text{SO}_2$ , free  $\text{O}_2$ ,  $\text{SO}_3$  and a grey white deposit part of which is free sulphur. This substance absorbs moisture when exposed, does not fume, and gave negative results when examined for persulphate.

## 14. Equilibrium in the system: Sodium Sulphite-Sodium Thiosulphate-Water.

S. G. KIRI and K. R. KRISHNASWAMI, Bangalore.

After carrying out preliminary experiments in order to ascertain the most suitable form of apparatus and conditions for analysis, the composition of the equilibrium mixtures obtained at various temperatures were determined. The results are discussed.

Determinations were also made of the solubility of sodium thiosulphate in sulphite solutions of various concentrations at different temperatures and the results obtained are discussed.

## 15. The decomposition of Chromates at high temperatures.

V. T. ATHAVAL, Bangalore.

1. The vapour pressure curve of lead chromate shows breaks at  $650^\circ$ ,  $854^\circ$ , and  $920^\circ$ . The latter two correspond with the melting points of the compounds  $\text{Pb}_7\text{Cr}_2\text{O}_{13}$  and  $\text{Pb}_2\text{CrO}_5$  (Jæger and Germs, *Z. anorg. Chem.*, 1919, **119**, 155).

2. The vapour pressure curve of strontium chromate (m.p. with decomposition  $1160^\circ$ ) up to  $1400^\circ$  was studied in a molybdenum wire wound furnace and shows three breaks at  $945^\circ$ ,  $1257^\circ$ , and  $1375^\circ$ . These correspond with 50, 66.6, and 75 per cent. decomposition according to the equation  $2\text{SrCrO}_4 = 2(\text{SrO}), \text{Cr}_2\text{O}_3 + 3\text{O}$ ; the corresponding intermediate compounds being (A)  $4\text{SrO}, 2\text{CrO}_3, \text{Cr}_2\text{O}_3$ , (B)  $3\text{SrO}, \text{CrO}_3, \text{Cr}_2\text{O}_3$ , and (C)  $8\text{SrO}, 2\text{CrO}_3, 3\text{Cr}_2\text{O}_3$ . A and B are decomposed by acetic acid giving



insoluble residues of  $\text{Cr}_2\text{O}_3$  and  $\text{SrO}$ ,  $\text{Cr}_2\text{O}_3$  respectively. *A* and *B* have been isolated by heating strontium chromate in a high vacuum at  $1000^\circ$  and  $1200^\circ$ .

3. At  $1200^\circ$  in a vacuum, barium chromate decomposes to  $4\text{BaO}$ ,  $2\text{CrO}_3$ ,  $\text{Cr}_2\text{O}_3$ .

## 16. A rapid volumetric method for the estimation of Nitrite.

K. M. PANDALAI and G. GOPALA RAO, Waltair.

An iodometric method for the estimation of amounts of nitrites within  $\pm 0.25\%$  depending on the reaction  $2\text{HNO}_2 + 2\text{HI} = 2\text{H}_2\text{O} + \text{I}_2 + 2\text{NO}$  is described. The liberated nitric oxide tends to be oxidized to nitrogen peroxide in the presence of air and the nitrogen peroxide thus formed dissolves and liberates more iodine from the acidified potassium iodide. Hence the results for the nitrite will be variable and the following procedure is formulated: About 20 c.c. of the nitrite solution is taken, 4 gms. of sodium bicarbonate added, and then 5 c.c. of a 10% potassium iodide solution and a little starch solution. Now a rapid stream of carbon dioxide is bubbled through this reaction mixture for about ten minutes to eliminate oxygen. After acidifying with 10 c.c. of 0.5 *N* oxygen-free sulphuric acid, iodine is titrated against standard thiosulphate solution. The carbon dioxide liberated from the bicarbonate present will expel the nitric oxide as soon as it is formed.

## 17. The Electrometer valve.

D. N. MEHTA and S. K. KULKARNI JATKAR, Bangalore.

The paper describes the use of an electrometer valve (with a grid current of about  $10^{-14}$  amp. and grid insulation resistance of  $10^{15}$  ohms and having a working slope of 0.08 mil. amp. per volt) resistance coupled to valve of ordinary type as a null instrument in measuring the potentials of glass and antimony electrodes.

## 18. Isolation of the Mercury lines in the violet and the ultraviolet.

B. K. VAIDYA, Bangalore.

Light filters for the isolation of the groups of strong, photochemically active radiations from the mercury arc lamp, are described from time to time by various workers. Not all of these are however satisfactory when such of the factors as, stability towards light, fair amount of monochromatism, convenience in handling and easy procurability together with maximum transmissibility, are considered. In view of these difficulties the existing filters for the violet and the ultraviolet lines of mercury are modified or completely revised, and the following are recommended.—

Aqueous solution of cobalt sulphocyanate for the  $404\text{ }\mu\mu$  line; Wratten ultraviolet filter, or aqueous solutions of either chromium sulphate or cobalt sulphate for the lines at  $365\text{ }\mu\mu$ ; aqueous para-nitrosodimethylaniline combined with cobalt sulphate for the line  $334\text{ }\mu\mu$ ; potassium chromate in water with either Chance's u.v. glass or a solution of cobalt sulphate for the group of lines at  $313\text{ }\mu\mu$ , and chlorine gas at six atmosphere pressure with either cobalt sulphate or a mixture of cobalt sulphate and nickel sulphate for the radiations at  $254\text{ }\mu\mu$ .

Concentrations and thicknesses of the various solutions, and the transmission data as recorded by the thermopile, as also the photographs of the mercury arc through these filters, are given.



19. An X-ray investigation of the crystals of *p*-hydrazotoluene.

MATA PRASAD and M. P. LAKHANI, Bombay.

The crystals of *p*-hydrazotoluene belong to the monoclinic prismatic class. From rotation photographs about the *a*-, *b*-, and *c*-axes the dimensions of the unit cell have been determined.

The oscillation photographs taken about the *a*- and the *b*-axes show that (*h*01) planes are halved when *h* is odd and (010) is also halved. These halvings correspond to the space group  $C_{2h}^{52}$  with  $\overline{1}m$  Bravais lattice. The number of molecules required by the space group is four and the number of molecules calculated from the dimensions of the unit cell and the density of the crystals being also four, the molecules are asymmetric.

A probable arrangement of molecules inside the unit cell has been suggested.

20. An X-ray investigation of the crystals of anthranilic acid.

M. R. KAPADIA and MATA PRASAD, Bombay.

The crystals of anthranilic acid occur in two modifications. Both of which belong to the Rhombic-bipyramidal class. They differ in the axial ratios and the density. From an x-ray investigation of the first modification (density 1.367), dimensions for the unit cell have been determined.

The discrepancies between the value of the axial ratio obtained by Groth have been explained.

The oscillation photographs taken about *a*- and *b*- axes gave a series of planes in which planes (*h*01) are halved when *h* is odd and (*h*k0) are halved when *k* is odd. The crystals thus belong to the space group  $Q_{11}^{11}$ . The number of molecules in the unit cell is eight. The molecules of anthranilic acid are, therefore, asymmetric.

21. An X-ray investigation of the crystals of *o*-Nitro Diphenylamine.

JAGDISH SHANKER and MATA PRASAD, Bombay.

The substance was prepared by the method described by Goldberg (*Ber.*, 1907, 4545), and was purified by recrystallization from alcohol. Two types of well defined crystals were obtained by the slow evaporation of an alcoholic solution of the pure substance: (i) hexagonal form, and (ii) rhombic form [Groth (vol. V, p. 49) describes only the first form]. The melting point of both the forms was the same, 77.5°.

The rotation photographs taken about *a*-, *b*-, and *c*-axes by means of a shearer gas tube fitted with a copper anti-cathode were found to be identical in both the forms of the crystals. The dimensions of the unit cell have been determined.

Oscillation photographs about *a*- and *b*- axes were taken at an interval of 15°, and the indices of the planes were worked out by Bernal's method (*Proc. Roy. Soc., A.*, 1926, 113, p. 117). It was found that planes (*h*01) are halved when *h* is odd and (*h*k0) are halved when *k* is odd. Also the planes (100) and (010) are halved. These halvings correspond to the space group  $Q_{11}^{11}$ . The number of molecules required by the space group is eight. The molecules, therefore, possess some elements of symmetry. A probable arrangement of molecules inside the unit cell has been suggested.



## 22. The magnetic properties of the system Sulphur-Selenium.

S. S. BHATNAGAR and P. L. KAPUR, Lahore.

The magnetic property of a non-metallic binary system, sulphur-selenium, with respect to concentrations up to 10 atoms per cent. of selenium has been studied. The susceptibility-concentration relationship provides a curve and not a straight line which would have been the case if it obeyed the additive law of Pascal for mixtures. The maximum deviation occurs at a point where sulphur and selenium exist in a definite ratio and it appears to be due to the formation of sulphur-selenium complex.

## 23. On the theory of liquids.

T. S. WHEELER, Bombay.

If  $\frac{\mu}{r^m}$  is the force between two molecules with the distance  $r$  between their centres,  $\mu$  being independent of temperature, and if  $\delta$ , the diameter of the molecule is taken to be given by

$$\delta = K_1 \sqrt[3]{V},$$

where  $K_1$  is a constant and  $V$  is the volume of 1 mol of the liquid, then it is shown that at low temperatures the surface tension  $\gamma$  is given by

$$\gamma = K_2 V^{\frac{m+1}{3}}.$$

If  $m$  be put equal to 11, we obtain

$$\gamma = K_2 V^4$$

which is the parachor equation.

From this, making use of the Gibbs-Helmoltz equation, it can be shown that

$$L_i = 8.24 \gamma V^{\frac{2}{3}} \left( 1 + \frac{7T\alpha}{3} \right)$$

where  $L_i$  is the internal heat of vapourization in calories per g.-mol, and  $\alpha$  is the coefficient of thermal expansion. The application of this equation shows good agreement with observed values.

## 24. Photo-reduction of Ferric Chloride in Alcohols.

B. V. MOHILE and MATA PRASAD, Bombay.

Photo-reduction of pure anhydrous ferric chloride in ultraviolet light from mercury arc lamp in solution in anhydrous alcohols has been studied. It is observed that the reaction proceeds in two stages.

The reaction in the initial stage follows a zero-molecular order. An equilibrium or a stationary stage is then reached after a certain time, depending upon the concentration of the solution. On further exposure the reaction begins again, the velocity in the second stage being greater than that in the first stage. Experiments are in progress to study the effect of concentration and pH on the course of the reaction.

## 25. Photolysis of Amides and Amines in sunlight.

K. M. PANDALAI and G. GOPALA RAO, Waltair.

Aqueous solutions of amides are photolyzed when exposed to sunlight in the presence of photo-sensitizers like zinc oxide and titanium dioxide. The first step in the reaction is hydrolysis resulting in the formation of the ammonium salt of the corresponding acid, e.g. from acetamide,



ammonium acetate is formed. The ammonia is then oxidized to nitrite if calcium carbonate is present.

Amines are oxidized to nitrite in aqueous solutions when exposed to sunlight in the presence of photo-sensitizers. Here also the first step in the reaction is hydrolysis resulting in the formation of the corresponding alcohols and ammonia. Alcohol is subsequently oxidized to aldehyde and the ammonia to nitrite.

Amides and amines undergo similar changes in the soil which are ascribed to bacteria. The authors suggest that these changes are not entirely due to bacterial action, but that they are also partly photo-chemical in character.

## 26. Absorption and dispersion in terpenes.

R. PADMANABHAN and S. K. KULKARNI JATKAR,  
Bangalore.

The absorption spectrum of nopinene and sabinene was studied with a Speckkar photo-meter. No band was found in the region where rotation dispersion was anomalous. In the case of nopinene the observer anomaly is apparently due to an impurity having a rotation of opposite sign and high dispersion repeated fractionation having yielded a substance having this property.

## 27. Surface tensions of aqueous salt solutions.

S. S. JOSHI and P. K. N. PANIKKAR, Benares.

It is shown that the surface tension of the solutions tends to be an ionically additive property as the salt concentration is diminished. No accurate relation could be traced between the molecular concentration of the solute and its effect on the surface tension of water. The results obtained show that the increase in the coagulating power of an electrolyte with an increase of its molecular weight cannot be ascribed to the capillary activity of the electrolytes which are studied.

## 28. A note on the current permeability theories and their application to the action of foreign substances on the permeability of membranes.

A. NAGARAJA RAO, Bangalore.

An attempt is made to explain the effects of foreign substances by considering the Sieve theory of Traube, the lipoid theory of Overton and the adsorption and surface tension theories. Changes in the structure of the micelle consequent on the adsorption of the foreign substances have also been explained.

## 29. Coagulation of colloid Aluminium Oxide by Potassium Chloride solutions.

S. S. JOSHI and P. K. N. PANIKKAR, Benares.

Gann (*Kolloid Chem. Beihefte*, 1916, 8, 64) showed that the above coagulations showed *autocatalysis* when examined viscometrically. In order to test the validity of his conclusions, viscosity measurements have been taken by Scrapa's apparatus which does not require a knowledge of the density to evaluate the viscosity. On varying the coagulation concentration, it was found that keeping the colloid content constant, the nature of the viscosity-time curve varied considerably with the coagulation concentration. The Scrapa curve characteristic of *auto-catalysis* was observed only in a very limited number of coagulations



and marked viscosity changes with time occurred without any sensible coagulation taking place.

30. Effect of ultraviolet rays on hydrophobe sols.

S. S. JOSHI and A. S. NANJAPPA, Benares.

The relation between viscosity and the coagulation of (i) antimony sulphide sol, (ii) thorium hydroxide sol, and (iii) colloidal manganese dioxide has been studied. The sols were exposed in a quartz vessel to the action of intense ultraviolet light and viscosity measured at definite intervals. No change in viscosity was observed in any case. Change in refractive indices and in absorption spectra of the solutions were measured to study coagulation, but no change in these physical properties was noticed. Sols of gum dammer and gamboge were also exposed but no change in their refractive indices were observed.

31. Kinetics of slow coagulation from the standpoint of Smoluchowski's theory.

S. S. JOSHI, Benares.

In a number of communications the author and his collaborators have shown that the actual process of coagulation of polydisperse sols in the slow region is much more complex than that contemplated in the Smoluchowski theory and is not amenable to a simple extension of the theory. Smoluchowski's theory does not take sufficient account of the precise role of the post primary particles, a factor involved in the autocatalysis theory of the kinetics of coagulation. One of the chief assumptions of Smoluchowski's theory is that coagulation is only a continued coalescence of the primaries. The evidence accumulated by the author shows that the process of coagulation is discontinuous with respect to time.

Another possibility ignored in the various theories of coagulation is the possible variation in the adsorbability of the coagulating material during coagulation. It is suggested that the change consists of *successive zones of coagulation* and that each such zone is characterized by a sensibly constant electrolytic adsorption. The theoretical utility of this postulate in affording a rational basis for the classification of coagulation into 'rapid' and 'slow' regions and offering a plausible interpretation of the Bödlander limit are discussed.

32. The variations of viscosity during the coagulation of the Antimony Sulphide and Ferric Oxide sols.

S. S. JOSHI and A. S. NANJAPPA, Benares.

The change in viscosity on the coagulation of antimony sulphide and ferric oxide sols has been studied. The antimony sulphide sol was treated with variously concentrated solutions of potassium oxalate, potassium tartarate, thorium nitrate, and potassium chloride; the ferric oxide sol was coagulated by ferric chloride, thorium nitrate and barium chloride. In agreement with previous results the viscosity-time curves show a number of marked discontinuities and in a number of cases a well defined initial fall. Judged both by the turbidity method and the occurrence of flocculation, coagulation was found to have been taking place in all these cases. In the majority of these experiments, it was found that the viscosity had diminished appreciably during the progress of coagulation, which is remarkable, being contrary to general experience. The concentrations of the coagulants used corresponded to the region of slow coagulation. It is also significant that the electrolyte added contained, in the majority of cases, polyvalent ions of the same charge as the colloid.



33. The variation of the refractive index of colloids subjected to coagulation in the slow region. Evidence for the existence of 'Zone of Coagulation'.

S. S. JOSHI and S. JAGA RAO, Benares.

Results are given for the change of the refractive index of colloid manganese dioxide when mixed with aqueous solutions of HCl,  $(\text{Li})_2\text{SO}_4$ , NaCl,  $\text{NH}_4\text{Cl}$ , KCl,  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{La}(\text{NO}_3)_3$ ,  $\text{Ce}(\text{NO}_3)_4$  and  $\text{Th}(\text{NO}_3)_4$ . The concentrations of each of these were varied over by wide range. On the whole the refractive index diminished during coagulation due to  $\text{Th}(\text{NO}_3)_4$ ,  $\text{AlCl}_3$ ,  $\text{NH}_4\text{Cl}$  in all the cases observed. With solutions of HCl, NaCl and KCl, at certain stages of coagulation, the refractive index increased beyond the initial value depending upon the concentration of the coagulation. The refractive index always increased during coagulation due to solutions of  $\text{BaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{La}(\text{NO}_3)_3$ . In almost all coagulations, a steady state was produced during which the refractive index remained constant over quite long periods.

Evidence is obtained showing that the change is not continuous in respect of time. Coagulation by  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{Ce}(\text{NO}_3)_4$ ,  $\text{Th}(\text{NO}_3)_4$  and  $\text{AlCl}_3$  revealed the existence of a number of exceedingly well defined stages during each of which the refractive index remained constant. It is considered that the existence of these stages, each marked by a characteristic refractive index, affords evidence for the theory advanced by Joshi that coagulation is not time-continuous, but occurs through successive zones of coagulation.

34. Variation of viscosity in the mutual coagulation of colloids.

S. S. JOSHI and P. K. N. PANIKKAR, Benares.

This has been investigated by the Scarpa's method for coagulation with the ferric oxide sol mixed with colloid (i) antimony sulphide, (ii) manganese dioxide, and (iii) arsenious sulphide. The proportions of the constituents of the mixtures were varied over a wide range. The viscosity-time curves showed definite discontinuities and in some cases an initial fall. In the system ferric oxide sol and arsenious sulphide sol, it was observed that the viscosity never increased beyond the initial value. In a series of coagulations between the sols of ferric oxide and arsenious sulphide viscosity never increased beyond the initial value. A diminution of viscosity through a series of breaks was also observed when there was no coagulation produced in the system. The common notion of viscosity rise during coagulation must be considered as unjustifiable by these and similar results observed in these laboratories.

35. Studies of some physical properties of gels in order to determine their structure. Part IV.

N. A. YAJNIK, D. N. GOYLE, and C. L. RAMPAL,  
Lahore.

Further work on the study of some physical properties of stannic phosphate, acetyl cellulose, thorium phosphate, silica and alumina gels has been carried out. The evidence collected so far points to the crystalline structure of gels with a regular arrangement of crystalline units in the case of elastic gels and an irregular and haphazard arrangement in the case of the nonelastic or brittle gels. The above view with regard to the structure of gels closely approximates to the view of the gel structure advanced by Wm. C. Arsem (*J. Phys. Chem.*, 1926, 306).



36. The relationship between H-ion concentration and adsorption.

N. A. YAJNIK, D. N. GOYLE, and ISHWAR DASS, Lahore.

Attempts have been made to investigate whether any relationship exists between the adsorption of dyes (acidic, basic, and neutral) from their solutions by various adsorbants (charcoal, silica, and neutral alumina gels) and the H-ion concentrations of the dye solutions. As a result of these investigations it has been found that—

- (1) the H-ions are greatly responsible for the process of adsorption,
- (2) in the case of the acidic and neutral dyes there is an increased adsorption of the dye with an increase in the H-ion concentration and vice versa,
- (3) in the case of the basic dyes there is a decrease in the adsorption of the dye with a decrease in the H-ion concentration,
- (4) on varying the concentration of the H-ions but keeping the concentration of the dye constant, the conclusions mentioned in 1, 2, and 3 have been arrived at.

A mechanism of the phenomena of adsorption is proposed.

37. Adsorption of electrolytes by activated charcoal with reference to its electrical charge.

S. P. ROYCHOUHDURY, Calcutta.

Electro-osmotic experiments of negatively and positively charged sugar charcoals in contact with increasing concentrations of HCl,  $\text{H}_2\text{SO}_4$ , NaOH, and NaCl have been carried out. With HCl and  $\text{H}_2\text{SO}_4$  the negative charge has been found to decrease while, with NaOH and NaCl, the negative charge increases. Positively charged charcoal acquires a negative charge with very low concentrations of HCl and  $\text{H}_2\text{SO}_4$ .

Analytical estimations of the adsorption of HCl,  $\text{H}_2\text{SO}_4$ , and NaOH have been carried out with both samples by different methods.

38. Heat of adsorption of Nitric Oxide by charcoal.

M. S. SHAH and S. G. SHARANGPANI, Ahmedabad.

The adsorption of nitric oxide by charcoal has been observed to proceed continuously for a long time accompanied with chemisorption of oxygen (Shah, *J.C.S.*, 1929, 2661). In studying the mechanism of the process, the heats of adsorption of nitric oxide, carbon dioxide, and nitrogen by purified sugar charcoal, which had been previously heated to  $900^\circ$  under a high vacuum, have been accurately measured under varying conditions at  $0^\circ\text{C}$ .

In experiments with nitric oxide, it has been observed that—

- (i) the evolution of heat is maximum at the commencement of adsorption,
- (ii) the evolution of heat is continuous and is proportional to the volume of the gas adsorbed by charcoal if the pressure of the gas is kept constant, and
- (iii) the evolution of heat goes on progressively diminishing with time when the adsorption is allowed to proceed with a definite volume of the gas.

In experiments with carbon dioxide and nitrogen, no such continuous evolution of heat is observed since the process of adsorption is complete within a short time.



## 39. Velocity of reactions in heterogeneous systems, Part II.

D. D. KARVÉ and K. K. DOLE, Poona.

The reaction between carbon disulphide and sodium hydroxide was studied further by using neutral solvents, immiscible in water. The velocity was found to be proportional to the carbon bisulphide concentration as well as to the alkali concentration. In the reaction of carbon bisulphide with aqueous alkali, increase in the quantity of the former increases the velocity up to a maximum limit, further increase having no influence.

## 40. Velocity of reactions in heterogeneous systems, Part III.

D. D. KARVÉ and K. K. DOLE, Poona.

The decomposition of benzyl chloride with water and the hydrolysis of benzyl acetate with  $N/100$  alkali have been studied. In the case of the former reaction, separation of benzoic acid, which is sparingly soluble in water introduced disturbing factors. When a solvent like xylene was used, the reaction conformed to the monomolecular formula. The hydrolysis of benzyl acetate gave similar results.

## 41. The electrical properties of colloidal solutions with reference to the difference between the colloidal solutions of acid substances and of acids in true solution.

J. N. MUKHERJEE, Calcutta.

Colloidal solutions of insoluble substances which are known from electrochemical data to have a decidedly weak character, behave as very strong (completely dissociated) acids, in a state of colloidal solution. Calculations show that they resemble univalent more than polyvalent completely dissociated acids. They also show the character of a weak partially dissociated acid.

The total neutralizable acid is determined by the specific surface and kinetic factors. Different forms of curves are obtained which show the variation of the hydrogen ion concentration with the dilution.

There is evidence showing the disappearance of hydroxyl ions by chemical combination with anhydride acid molecules as distinct from neutralization of hydrogen ions. It has also been observed that different quantities of the strong bases (e.g., NaOH and  $\text{Ba}(\text{OH})_2$ ) are required for the neutralization of the same amount of a colloidal acid.

The thermodynamic assumptions underlying the definitions of degrees of dissociation, dissociation constants and solubilities are not applicable without modification to these colloidal solutions. There is no standard state of reference and no unequivocal definiteness of the total concentration.

## 42. Difficulties in the measurement of the cataphoretic speed of colloidal particles by the moving boundary method.

J. N. MUKHERJEE, S. P. ROYCHOUDHURY, and  
S. PALIT, Calcutta.

In the present paper difficulties met with in the measurement of the cataphoretic speed of colloidal particles by the Moving Boundary Method, other than those directly arising out of the migration of ions under an electric field (e.g. calibration of the tube, separation of the boundary into two layers, free fall of the boundary, movement of colloid through the upper liquid, choice of a suitable upper liquid, constancy of the potential gradient) have been discussed.



The peculiarities of the free fall of the boundary have been discussed and it has been shown that the rate of free fall depends on the nature of the upper liquid, the dilution of the sol and the rate of filling the tube with the colloid. With the ultrafiltrate as upper liquid a ferric hydroxide sol exhibited no free fall. The free fall has been observed even when the differences of density between the upper liquid and the colloid is negligible.

Possibilities of the mechanical mixing, at the boundary of the upper liquid and the colloid, and also of disturbances of the adsorption equilibrium, or of the chemical equilibrium, e.g. changes in degree of hydrolysis on account of the difference in the nature and concentrations of the ions, have been discussed.

On the addition of electrolytes, the potential gradient between the side limbs has been observed to decrease considerably in the case of a ferric oxide sol although the potential drop between the electrodes and the positions of the latter were kept constant. Sometimes a small but regular change in the potential gradient takes place during the passage of the current. These effects probably arise from the adjustment of the concentrations of the two electrolytic solutions in the sense of Kohlrausch's theory of Moving Boundaries or from the changes referred to in the third paragraph above.

#### 43. Surface tension of colloids.

D. N. CHAKRAVARTI, Amraoti.

The surface tension of the following colloids has been determined by the methods of Richards, Jaeger, and DuNouy at different dilutions: (1) vanadium pentoxide, (2) mastic, (3) chromium tungstate, (4) zirconium hydroxide, (5) gum dammar, (6) ferric borate, (7) ceric borate, (8) ceric molybdate.

It is observed that the fall of surface tension is very little due to the presence of the dispersed phase specially with the methods of Richards and Jaeger. In some cases a considerable fall in the surface tension is observed when the measurement is made by DuNouy method. It may be concluded also from my results that there is no static or dynamic surface tension of colloids. A mathematical relation has been obtained correlating the surface tension and concentration of the sols.

#### 44. Viscosity variations of colloid Manganese Dioxide in the presence of non-electrolytes.

S. S. JOSHI and P. S. RAO, Benares.

Experiments are described showing the influence of non-electrolytes on the viscosity variations of coagulating colloids. The non-electrolytes added were solutions of urethane, methyl alcohol, ethyl alcohol, sucrose, and urea of various concentrations. With the exception of alcohol and sucrose, it was generally observed that, in the mixtures where no coagulation occurred, the viscosity remained reasonably constant. Conversely, cases were observed in which variation of viscosity continued in the mixture without any sensible coagulation. This is a striking support of the view, expressed elsewhere, that the determinants of viscosity change and of coagulation, need not necessarily be identical.

#### 45. Variation of the refractive index during mutual coagulation.

S. S. JOSHI and P. K. N. PANIKKAR, Benares.

Changes in refractive index have been investigated during the coagulation of colloid manganese dioxide by colloid ferric oxide. The curves



obtained are characterized by a final state after which the refractive index does not vary and by discontinuous intermediate stages indicative of a succession of zones of coagulation.

#### 46. The influence of concentration on the viscosity of colloids.

D. N. CHAKRAVARTI, Amraoti.

The viscosity has been determined at different concentrations. The equation of Einstein, Hess, Hatschek, and Arrhenius were tested with the experimental results on the following sols: (1) ferric hydroxide, (2) arsenious sulphide, (3) ceric hydroxide, (4) molybdic acid, (5) antimonie acid, (6) mastic, (7) chromium hydroxide, (8) aluminium hydroxide, (9) gum dammar, (10) ferric phosphate, (11) zirconium hydroxide, (12) chromium arsenate, (13) ferric tungstate, (14) ferric arsenate, (15) vanadium pentoxide, (16) chromium tungstate, (17) zirconium hydroxide, (18) ferric borate.

The values of hydrations were calculated for these sols at different concentrations. It was found that the constant 2.5 in the Einstein equation changes from 1.23 to 3.13 with different sols. The dead space 'a' in Hess' equation does not remain constant at different dilutions but is found to be proportional to the viscosity of the sols.

#### 47. Electrical dispersion of liquids.

S. PARAMASIVAN, Madras.

Some interesting phenomena in electrical dispersion of liquids are observed when a current of electricity passes through a system composed of two immiscible electrolytes. Not only the ions but also the electrons and solvated ions are responsible for the transference of electricity from one electrolytic phase to the other.

#### 48. Viscosity of dilute solutions of non-electrolytes.

BALBHADRA PRASAD, Cuttack.

The logarithm of viscosity plotted against the logarithm of vapour pressure of a liquid gives a straight line. The law connecting viscosity and temperature can be derived from the above generalization. This law is found to be valid for non-associated liquids as found by a number of workers. The author found that as in the case of pure liquids, the logarithm of viscosity of solutions plotted against vapour pressure of the solution concerned or the pure solvent gave a straight line which is for all practical purposes parallel to the line obtained for the pure liquid. Taking this fact and the law connecting vapour pressure of a solution and its concentration into account, an equation connecting viscosity and concentration is derived. This equation is of the form  $\frac{\eta}{\eta_0} = 1 + \alpha c$  where  $\eta$  is the viscosity of the solution,  $\eta_0$ , that of the pure solvent and  $\alpha$  is a constant which is independent of the solute and temperature.

Experiments carried in this laboratory show that  $\alpha$  is independent of temperature.

#### 49. Variability of the numerical value of Traube's factor with changes in the concentration of the examining solution.

A. C. CHATTERJI, Lucknow.

Freundlich, basing his observation on Langmuir's explanation of Traube's rule, states that the numerical value of the factor is 3.3.



From the experiments given in a previous paper, it has been found that the factor varies with the concentration of a particular pair of any homologous series as well as with the molecular weight of the pair.

In the case of the alcohols, the factor varies from 3.9 to 5, whereas with fatty acids it changes from 3 to 4.2.

It has been found that, both for the alcohols and fatty acids, the factor reaches a maximum value for the ninth or the tenth member and then declines.

## 50. Applicability of Traube's rule to the phenomenon of wettability.

A. C. CHATTERJI, Lucknow.

The amount of wettability of known substances like naphthalene, anthracene, phenanthrene by watery solutions of fatty acids, alcohols, esters, and amines has been measured by means of a simple apparatus devised in Traube's laboratory.

It has been shown that, in a homologous series, the wettability increases from member to member with increasing molecular weight.

It has been proved that Traube's rule holds good in the following cases :—

- (a) Wettability of anthracene by solutions of fatty acids.
- (b) Wettability of naphthalene by alcohol solutions.
- (c) Wettability of phenanthrene by solutions of esters.
- (d) Wettability of naphthalene by amines in watery solution.

In the case of fatty acids and anthracene, the well known Traube Factor has been shown to be about 3, whereas with alcohols it varies. In the case of amines the factor has been found to be 2, which is in agreement with the observations of Freundlich from experiments in an entirely different line.

In the case of higher members of the fatty acids and alcohols the factor becomes somewhat smaller.

## 51. Effect of polar and non-polar organic compounds on the wettability of a substance.

A. C. CHATTERJI, Lucknow.

The effect of the following organic compounds has been investigated :—

- (a) Oleic acid, aniline, toluidine, xylydine, phenol, benzyl alcohol.
- (b) Paraffin (both liquid and solid), carbon disulphide, carbon tetrachloride, chloroform, pentane, hexane.

It has been found that polar compounds in small quantities increase the wettability to a great extent whereas non-polar compounds, even in considerable quantities, produce very little effect.

A new method for determining wettability has been devised.

## 52. On the Resorption of Calcium Salts through Membranes. I. On the Influence of the Acid Radicle on the Resorption of Calcium Salts through Membranes.

A. NAGARAJA RAO, Bangalore.

In this series of experiments the diffusion of a number of calcium salts of different organic acids through an animal membrane (intestinal membrane of a pig) has been measured. It has been observed that there is no direct proportionality existing between the size of molecule (without taking into consideration its hydration) and the amount of the substance



diffused although several factors other than the mere size seem to play a more important part. The influence of capillary active substances has also been investigated.

### 53. On the Influence of Foreign Substances on the Diffusion of Dye-stuffs through Gels. I.

A. NAGARAJA RAO and B. S. BHEEMA RAO, Bangalore.

Capillary-active and hydrotropic substances are found to alter the diffusion of acids and sugar through membranes and gels. Qualitative experiments using gelatine gels have also led to a similar conclusion in the case of the permeation of dye-stuffs through them. A plausible explanation of the phenomenon would be by a consideration of the changes in the wetting of the pore walls caused by the adsorption of the foreign substance. Factors like swelling, the structure of the micelle leading to an altered pore-size, and the changes in the degree of dispersion of the dye-stuff itself are also to be considered before a conclusive explanation could be offered.

### 54. Constitution of Iodic acid and Iodates from Raman Spectra.

M. R. NAYAR and P. N. SHARMA, Lucknow.

In a previous communication it was pointed out from a study of freezing point depressions and conductivity measurements that iodic acid in concentrated solution is polymerized, but in dilute solutions it has the simple formula,  $\text{HIO}_3$ , and that iodates are salts of a monobasic acid.

This has now been confirmed by a study of the Raman spectra of solutions of iodic acid of varying concentrations. Raman frequency shifts approximately corresponding to

840	670	346	1860 cm. <sup>-1</sup> .
(very strong)	(strong)	(medium)	(faint)

Besides, a few other less prominent lines have been obtained with 5N iodic acid. These lines become fainter or totally disappear with dilution, while the water bands become more diffuse and intense.

The results are compared and discussed with those obtained by Nisi and by Krishnamurti.

### 55. The Raman effect in monobasic fatty acids.

G. V. NEVGI, Bangalore.

Raman spectra are obtained for (1) *n*-butyric acid, (2) *iso*-butyric acid, (3) isovaleric acid, (4) *n*-caproic acid, (5) isocaproic acid.

In all the acids, the C-H longitudinal oscillations are represented by three prominent frequencies at 2870, 2910, and 2940. The frequencies 1450 and 1300 are due to the transverse oscillations of hydrogen of the  $\text{CH}_3$  and  $\text{CH}_2$  group respectively. According to Collins, the frequency 1060 in alcohols represents the oscillation of the carbon chain as a whole, but its appearance in acids also and its agreement with the calculated value (1045) show that it may be due to the aliphatic C=O linkage present in acids, alcohols, and ethers. The frequency 1650 is due to the vibration of carbon and oxygen of the C=O linkage in the carboxyl group.



## 56. Raman spectra of some substituted benzene derivatives.

G. V. NEVGI, Bangalore.

The Raman effect has been investigated in the following compounds: (1) *n*-propyl benzene, (2) *isopropyl* benzene, (3) *p*-cymene, (4) indene, (5) veratrol, (6) mesitylene.

*n*-propyl benzene and *isopropyl* benzene are monosubstituted, *p*-cymene—a para-disubstituted, indene and veratrol—ortho-disubstituted, and mesitylene—a trisubstituted benzene derivative. The characteristic benzene ring frequencies in these compounds have been determined.

The results show that all the ring frequencies are reproduced in the monosubstituted compounds. In the disubstituted derivatives, the 1000 frequency is missing in all three and 1030 is observed only in ortho-compounds, with a slightly higher value in veratrol. In the trisubstituted derivative, mesitylene, the two frequencies 1000 and 1030 should be much fainter than in the disubstituted, but they are as strong as in benzene which is evidently due to the symmetrical ring structure common to both benzene and mesitylene. In mesitylene, the frequencies 235, 280, 580, and 1000 appear also as anti-Stokes lines. The frequency 1167 in veratrol is due to the aromatic C=O linkage (calculated value=1162).

## 57. Raman Effect in Santalols.

B. SANJIVA RAO, Bangalore.

Santalols have been prepared with rotations  $+6.4^\circ$  and  $-45.0^\circ$  and their Raman spectra compared. The spectra resemble each other though certain interesting differences have been noticed.

## 58. The structure of molecular compounds.

BALWANT SINGH and H. B. DUNNICLIFF, Lahore.

The structure of some molecular compounds has been studied by the parachor method. It has been found that one of the components of the molecular compound acts as a donor and the other as an acceptor so that a co-ordinate link is formed between them.

## 59. The molecular structure of ortho-substituted benzene derivatives in solution.

BALWANT SINGH and H. B. DUNNICLIFF, Lahore.

The parachors of a number of ortho-substituted benzene derivatives have been determined in benzene solution at  $28^\circ\text{C}$ . by the method of Hammick and Andrew (*J. Chem. Soc.*, 1929, 754). The values obtained establish the occurrence of intra-molecular co-ordination which results in the formation of an ortho-ring in each of the compounds.

## 60. The Physical Identity of Enantiomers. Part I. The Rotatory Dispersion of Enantiomeric Camphors and Camphoric Acids.

B. K. SINGH and INDRAMANI MAHANTI, Cuttack.

Campbell (*J. Amer. Chem. Soc.*, 1930, 26, 560; 1931, 53, 1661) noticed differences in the numerical values of the rotatory powers of *d*- and *l*-camphoric acids. We have re-examined the rotatory power for 10 different wavelengths ( $\lambda=4358$  to  $6708$ ) of the carefully purified specimens of *d*- and *l*-camphoric acids and found them to be identical,



thus confirming Pasteur's Law of Molecular Dissymetry. It appears that the discrepancies noticed by Campbell were due to differences in the degree of purity of the two forms.

The camphoric acids obey the law of simple dispersion, whereas camphor follows that of complex dispersion (cf. also Lowry, *J.C.S.*, 1925, 127, 604).

61. Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XXI. Stereoisomeric Nitrobenzalaminomethylenecamphors and para-dimethylamidobenzalaminomethylenecamphor.

B. K. SINGH and S. C. SEN, Cuttack.

Nitrobenzaldehydes (*o*, *m*, *p*) and para-dimethylaminobenzaldehyde have been condensed with aminomethylenecamphors (*d*, *l*, *dl*) in methyl alcoholic solution in presence of anhydrous sodium sulphate. The optically active isomerides (*d* and *l*) have identical rotation and are found to obey the simple dispersion law of Drude,

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}.$$

From such a study we notice that the molecular rotation of these compounds does not bear any relation to the respective dissociation constants of the benzoic acids derived from the aldehydes employed as shown by Betti (*Gazzetta*, 1923, 53, 424). The influence of the solvents and of the position isomerides on the rotatory power are also discussed.

62. Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XXII. Rotatory Dispersion of Isonitroso-*d*-camphor and its Sodium Derivative.

B. K. SINGH and SHEONATH PRASAD, Cuttack.

Rotatory dispersion ( $\alpha$ ) of isonitroso-*d*-camphor has been determined for various wavelengths ( $\lambda$ ) and obeys Drude's Law of Simple Rotatory Dispersion,

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}.$$

The sodio-derivative is water-soluble and is being studied with a view to determine the difference in the physiological activities of dextro, laevo and racemic forms.

63. Resolution of Co-ordinated Inorganic Compounds into optical isomers. Part 2. Resolution of tri-ethylene-diamino-zinc chloride, bromide, iodide, and sulphate.

P. NEOGY and G. K. MUKHERJEE, Calcutta.

Using *d*-sodio-camphor-nitronate, tri-ethylene-diamino-zinc chloride, bromide, iodide, and sulphate have been obtained in the solid condition. The preparation of these active compounds in solution was reported to the last session of the Congress.



64. Resolution of Co-ordinated Inorganic Compounds into optical isomers. Part 1. Resolution of tri-ethylene-diamino-Cadmium chloride, bromide, iodide, and sulphate.

P. NEOGY and G. K. MUKHERJEE, Calcutta.

Attempts at resolution of compounds containing ethylene-diamine complexes of divalent metals like Ni, Zn, Cd, etc. have all along failed (Bucknall and Wardlaw, *J.C.S.*, 1928, 2739) though tris-dipyridyl compounds of divalent metals have been resolved by Werner (*Ber.*, 1912, 45, 433), Morgan and Burstall (*J.C.S.*, 1931, 2213). It has been shown here that using *d*-sodio-camphor-nitronate, tri-ethylene-diaminocadmium salts may be resolved. In this way the dextro chloride, bromide, iodide, and sulphate have been prepared and their rotations measured.

65. Reaction between Ammonia and Methyl Iodide to form Methylamine-hydroiodide.

J. C. GHOSH and A. R. RAO, Dacca.

The reaction  $\text{CH}_3\text{I} + \text{NH}_3 = \text{CH}_3\text{NH}_2 + \text{HI}$  proceeds fairly rapidly at temperatures between  $18^\circ$  to  $30^\circ$ , if the total pressure of the reactants exceeds a limiting value of about 24 cms. When the partial pressures of the reactants were each of the order of 10 cms. or less the reaction takes place with measurable velocity above  $325^\circ$ .

In the low temperature reactions, the reaction came to an end when the pressure inside the reaction tube was of the order of 24 cms. This is explained as being due to the vapour pressure of a liquid film of methyl iodide saturated with methyl-aminehydroiodide at the temperature of the reaction.

The low temperature reaction is a heterogeneous one which takes place in a liquid film of methyl iodide saturated with methylamine hydroiodide. An equation for the velocity of transformation has been obtained.

The reaction taking place above  $325^\circ$ , the total pressure of the reactants remaining below about 20 cms., follows the simple bimolecular equation law and the reaction is not influenced by an increase in the ratio surface : volume.

The reaction is sensitive to gaseous catalysts being pronouncedly influenced by iodine vapour.

66. Kinetics of Heterogeneous Organic Reactions. The Reactions between Organic Halogen Compounds and Solid Inorganic Salts.

M. V. NABAR and T. S. WHEELER, Bombay.

The work on the kinetics of the reaction between benzyl chloride or bromide and solid silver nitrate in presence of inert solvents has been continued. The rate of reaction with petroleum ether and ethyl ether is approximately the same, but it is increased in the presence of carbon tetrachloride. In chloroform the reaction is slow. Benzene appears to inhibit the reaction. The best constant is obtained by assuming a bimolecular reaction to take place. The presence of traces of copper decreases the velocity of the reaction greatly.

67. The decomposition velocities of substituted naphthol ethers when heated with halogen acids.

G. B. KOLHATKAR and V. V. BAPAT, Poona.

A large number of the ethers of substituted  $\alpha$  and  $\beta$  naphthols dissolved in glacial acetic acid are heated in the presence of an excess



of concentrated halogen acids on a boiling water bath. The decomposition velocity was ascertained by estimating either the naphthols liberated during the reaction or the undecomposed ether, after a definite interval of time. The concentration of the halogen acids being in large excess, the velocity constants are determined on the assumption that the reactions are uni-molecular. The values of the velocity constants obtained are fairly constant and thus justify the assumption.

A comparison of the velocity constants reveals the following relations:—

- (1) The velocity constants of the substituted ethers of both  $\alpha$  and  $\beta$  naphthol have a lower value than those of the ethers of  $\alpha$  and  $\beta$  naphthol.
- (2) The extent of the lowering in the velocity constants depends (i) on the nature, (ii) on the number, (iii) on the position of the substituting group.
- (3) The velocity constant, as in the case of simple ethers, greatly depends on the nature of the halogen acid employed.

#### 68. Influence of acidity and temperature on the hydrolysis of sugars.

A. V. VARADARAJA IYENGAR and S. RAJAGOPAL, Bangalore.

A preliminary study on the effect of pH on the hydrolysis of sucrose has been made. The time and temperature factors also have been considered. The determination of maltose, singly and in combination with sucrose, based on the above factors is in progress. The necessity for the addition of buffers has also been studied. The possible applications of the above in developing an accurate method of estimating carbohydrates in plant extracts and saps is indicated.

#### 69. The Kinetics of Heterogeneous Organic Reactions : A Study of the Benzoin Reaction.

D. R. NADKARNI, S. M. MEHTA, and T. S. WHEELER, Bombay.

The reaction of pure potassium cyanide on pure benzaldehyde in absence of a third substance gives benzoin but is inhibited in the presence of quinol, alkali halide, and other anticatalysts of the oxidation of benzaldehyde. The kinetics of this reaction has been studied at 100° and at ordinary temperature and found to conform to the equation :

$$\text{Rate of benzoin formation} = K_1 \cdot (\text{benzaldehyde})^2 \cdot (\text{benzoin}) + K_2 \cdot (\text{benzaldehyde})^2 \cdot (\text{potassium cyanide}).$$

It is suggested that the following two reactions take place :

(i) A heterogeneous reaction between solid cyanide and benzaldehyde, the 'cyanidion' on the surface of the solid cyanide being the effective agent. This reaction is inhibited by such negative catalysts as are adsorbed on the solid cyanide.

(ii) A homogeneous autocatalytic reaction between benzaldehyde and a trace of potassium cyanide dissolved in the benzaldehyde, which is uninfluenced by inhibitors as in (i).

The kinetics has also been studied in presence of water, when the rate of (ii) has been found to be unaffected but the reaction with solid cyanide is replaced by a reaction in which 'cyanidions' are involved. In this case reaction (ii) is more rapid at first but with the increase of the amount of water, the dissolved cyanide is extracted from benzaldehyde and hence ceases altogether after a time, reaction (i) alone predominating.

Current theories are discussed in the light of the above results and a mechanism is suggested.



70. The Decarboxylation of  $\beta$ -1-aryl-glutaric acids.

D. B. LIMAYE and GOVIND R. KELKAR, Poona.

The  $\beta$ -2-methoxy-4-methyl-phenyl glutaric acid obtained by the reduction of the corresponding glutaconic acid was subjected to (1) simple distillation, (2) distillation with lime, and (3) distillation with copper powder. From the resulting products nothing definite has yet been isolated.

Heating with hydrochloric acid in a sealed tube at 125–130° produces no appreciable change. Heating at 150–160°, however, yields 7-methyl-3:4-dihydro coumarin-4-acetic acid (m.p. 112–114°) identical with that prepared by Sheshadri by the action of cynacetamide on the coumarin. No decarboxylation has thus taken place in the process.

Methylation of the above acid gives back the original glutaric acid owing to the opening of the pyrone ring.

The dihydro-coumarin-4-acetic acid (b.p. 220°/5mm.) when distilled at atmospheric pressure yields a viscous liquid from which acetic acid and 7-methyl-coumarin have been isolated. The latter was found to be identical with that prepared from *m*-cresol and malic acid.

The elimination of acetic acid instead of simple decarboxylation is noteworthy.

## 71. Studies in Walden Inversion. Interconversion of the Tartaric acids.

V. ANNA RAO and P. C. GUHA, Bangalore.

*d*-Tartaric acid can be converted into a minute amount of *l*-tartaric acid by the Walden inversion of the dichloro derivative. Diethyl *meso* tartrate does not furnish an optically active product by hydroxylation of the corresponding halogen derivative. *l*-Chloromalic acid gives with potassium hydroxide *l*-tartaric acid. The sulphito ether of diethyl *meso* tartrate (b.p. 166°/9 mm.;  $D_{20}=1.324$ ,  $D_{25}=1.323$ ) yields the *meso* acid when hydrolysed either by dilute acid or alkali. Based on the results of hydrolysis of sulphito ethers of *meso* and *d*-diethyl tartrate their configurations have been elucidated. Walden inversion of the active menthyl ester of *meso* tartaric acid (m.p. 58°–59°, not an oil as recorded by Patterson and Kay, J. 1907, 91, 707) gave interesting results.

## 72. An Anomalous Benzoin Benzil Change.

K. M. PANDALAI, Waltair.

Whereas benzoin reacts with aniline and aniline hydrochloride to give (1) benzoin anilide, (2) benzoin anilide, and (3) diphenyl indole under different experimental conditions, it has not yet been shown that benzil is also formed together with small quantities of diphenyl at any particular intermediate stage. It has now been found that under suitable conditions benzil and diphenyl could be isolated from the reaction mixture, the former in good yields. It should be admitted that aniline—aniline hydrochloride mixture has no oxidizing action on secondary alcoholic groups as the effect observed with benzoin could not be duplicated so as to get other similar  $\alpha$ -diketones such as cuminil, anisil, piperil, furil, etc. from their corresponding secondary alcohols. This apparently anomalous action may be attributed to the highly tautomeric nature of benzoin as instances of its behaving in several reactions as *isobenzoin*, its enolic tautomer, are not uncommon. There seems to be a distinct relation between the nature of the reaction products and the enolizing



power of benzoin and oxidation proceeding through enolic tautomer. Literature on the reactivity of benzoin is given.

### 73. Photolysis of Aminoacids in Sunlight.

G. GOPALA RAO, Waltair.

Dilute aqueous solutions of aliphatic  $\alpha$ -amino acids decompose when exposed in glass vessels to sunlight in the presence of photo-sensitizers like zinc oxide and titanium dioxide. The products of decomposition are ammonia, carbon dioxide and an aldehyde containing one carbon atom less than the amino acid.

The ammonification of aromatic amino acids proceeds much less readily than those of aliphatic amino acids.

The ammonification of amino-acids proceeds in soil and is considered to be entirely due to the action of bacteria and fungi. The results recorded here indicate that ammonification in soils is also photochemical. It has also been found that aqueous solutions of proteins like albumin, casein and gelatin decompose in sunlight under aseptic conditions, with the slow liberation of ammonia.

### 74. Photoinversion and Photodecomposition in Geometrical Isomers, and the Energy levels of a *cis* and a *trans* molecule.

B. K. VAIDYA, Bangalore.

The interconversion of the geometrical *cis* and *trans* isomers in the presence of ultra violet light is well known.  $\alpha$ - $\beta$ -dibromocinnamic acid is, however, an exception. Both the *cis* and the *trans* forms of this acid are decomposed in light with the production of oily dibromostyrene and carbon dioxide. The electrical conductivity of this pair of isomeric acids also shows a contrast with other geometrical isomers, inasmuch as it does not show any very great variation from one form to the other.

Thus the behaviour of  $\alpha$ - $\beta$ -dibromocinnamic acid is anomalous even when compared with the very similarly constituted  $\alpha$ -monobromo acid. The presence of a second bromine atom in the molecule profoundly modifies its character, so far as the stability towards the light is concerned. It is possible that the centre of photoactivity is shifted in this molecule from its normal position in the  $C=C$  group to the  $-COOH$  group.

The theories of Mullikan and Olson regarding the energy levels of a *cis* and a *trans* molecule are examined in the light of the experimental evidence obtained from the quantum efficiency measurements of the various *cis* and *trans* isomers.

### 75. Conditions Governing the Formation of Geometrical Isomerides. Part I. The Stereoisomeric $\alpha\beta$ -Dibromocinnamic acids.

P. RAMASWAMI AYYAR, Bangalore.

Whereas addition of bromine to  $\beta$ -phenylpropionic acid yields a mixture of the *cis* (m.p.  $100^\circ$ ) and *trans* (m.p.  $136^\circ$ ) isomers, in the proportion of about 3:2, addition of bromine to the methyl ester of  $\beta$ -phenyl propionic acid and subsequent hydrolysis of the addition product yields much less *cis* than *trans*, the proportion being approximately 1:3.



76. Studies in the Isomerism of the Higher Unsaturated Fatty Acids and their Derivatives. Part II. A new isomeric Oleic acid ( $\Delta 8 : 9$ ) occurring in the Fatty acids of the *Garcinia* Fats.

P. RAMASWAMI AYYAR and J. D. VASAVADA, Bangalore.

The substance (m.p.  $14-15^\circ$ ;  $n_D^{23} = 1.4609$ ) has been isolated by the fractional precipitation of its lead salt from alcohol and petrol and yields capric acid ( $C_{10}H_{20}O_2$ ) and suberic acid ( $C_8H_{14}O_4$ ) on complete oxidation. Mild oxidation gives a dihydroxy acid, m.p.  $121-122^\circ$ .

77. Isomerism in Chloralides.

N. M. SHAH and R. L. ALIMCHANDANI, Dharwar.

The geometrical isomerism of the chloralides derived from  $\alpha$ -hydroxy carboxylic acids has been investigated. Two distinct forms, with sharp difference in m.p., have been isolated from the product of reaction of chloral hydrate with *d*-tartaric acid, *dl*-tartaric acid and lactic acid. In view of these results, the discrepancies of recorded melting points in literature are understandable and can be rectified.

78. Some Derivatives of Nitro *isobutylglycerol* (2-Nitro-2-methylol-propandiol-1:3). Part II. The triacetyl- and amino-derivatives.

K. C. PANDYA, Agra.

The preparation of nitro *isobutylglyceryl* triiodide has not been successful. The following are described: nitro *isobutylglyceryl* triacetate, rhombic crystals, m.p.  $76^\circ$ , amino *isobutyl glycerol* hydrochloride, m.p.  $149^\circ$ , hydrochloride of amino *isobutyl glyceryl* trichloride, m.p.  $260^\circ$  (decomp.) and the free base, m.p.  $180^\circ$  (decomp.), amino *isobutyl glyceryl* tribromide hydrochloride, m.p.  $220^\circ$  (decomp.).

Amino *isobutyl glycerol* could not be isolated in a pure condition as it suffered decomposition in contact with air.

79. The Action of Thionyl chloride on Penta-erythritol.

K. C. PANDYA, Agra.

Penta-erythrite-tetrachloride was obtained by Fecht (*Ber.*, 40, 3888) by the action of phosphorus pentachloride on pentaerythritol at  $150^\circ$ , but it can be obtained in a quick and easy way in very good yield by the action of thionyl chloride in the presence of pyridine. The product agrees in m.p. ( $96-97^\circ$ ) and is confirmed by analysis.

When thionyl chloride is used alone without any tertiary base, another white crystalline substance is obtained, soluble in alcohol, benzene, chloroform, more in hot chloroform. It melted at  $153.4^\circ$ . The presence of sulphur was found in the compound and analysis (by P. N. Kurien) showed sulphur to be 27.80%. This would accord well with the formula  $C_5H_8O_6S_2$  (28.07% S) pentaerythrite-disulphate which has been prepared by Baugault by the action of  $S_2Cl_2$  (*Cr.*, 123, 187).

The disulphate ester is also formed in the presence of ether.



80. A Study in the Degradation to Succinic acids through  $\gamma$ -butyro-lactones and other reactions of  $\beta$ -Anisyl- and  $\beta$ -Halogen-anisyl glutaric acids.

D. B. LIMAYE and R. G. CHITRE, Poona.

Windaus and Klanhardt have developed a method for the identification of  $\beta$ -alkyl substituted glutaric acids by the action of iodine on the silver salts when the  $\gamma$ -butyro-lactones are formed. (*Ber.*, 54, 581-587).

The method has now been extended to  $\beta$ -4-anisyl-glutaric acid (m.p. 164°).

Instead of the expected lactone,  $\beta$ -3-iodo-4-anisyl glutaric acid (m.p. 161°) was formed. 3-Bromo (m.p. 147°) 3-chloro (m.p. 157°)-4-anisyl glutaric acids also did not react.

However,  $\beta$ -3 : 5-dibromo-(m.p. 211°) 3 : 5-dichloro (m.p. 194°)-4-anisyl glutaric acids gave the corresponding  $\gamma$ -butyro lactones.  $\beta$ -3 : 5 dibromo-4-anisyl  $\gamma$ -butyro lactone (m.p. 98°), 3 : 5-dichloro (m.p. 72°).

The lactones on oxidation gave 3 : 5-dibromo (m.p. 198°) and 3 : 5-dichloro (m.p. 173°)-4-anisyl succinic acids, which have also been prepared by directly halogenating the corresponding succinic acid.

By condensing oxalic ester with diethyl esters of the above glutaric acids, the corresponding diethyl esters of 2-R-4 : 5-diketo-penta-methylene-1 : 3-dicarboxylic acids were prepared. (*Ber.*, 1899, 1932-35). R=4-anisyl (m.p. 123°), 3-iodo-4-anisyl (m.p. 133°), 3-bromo-4-anisyl (m.p. 128°), 3-chloro-4-anisyl (m.p. 126°), 3 : 5-dibromo-4-anisyl (m.p. 168°), 3 : 5-dichloro-4-anisyl (m.p. 165°).

Anhydrides, diethyl and dimethyl esters, semi-anilides phenacyl esters and oxidation products of the above glutaric acid were also prepared.

81. Structure of Benzene.

P. C. GUHA, Bangalore.

A new dynamic formula is now proposed according to which all the six carbon atoms of benzene lie in the first phase in one plane and in the second, alternate carbon atoms occupy positions in two parallel planes as suggested in the *Proceedings of the 19th Indian Science Congress*, 1932, p. 185. The model in both of its plane and solid phases is symmetrical and is in agreement with orientation results and number of possible derivatives. Oscillation of the carbon atoms, arrangement of bonds in different phases, evidence in support of *para*-linking, non-olefinic nature, etc. are discussed. Last of all are described the essentials from physical points of view, e.g. spectroscopic results, infra-red and Raman spectra, thermochemical data, X-ray and dipole moment, which the new model satisfies.

82. Halogenation, XVIII. Bromination and Iodination of Thymol.

P. S. VARMA, Benares.

Attempts have been made to brominate and iodinate thymol under different conditions of temperature, using various solvents and brominating and iodinating agents in the presence or absence of third substances. Experiments have been carried out using such solvents as acetic acid, alcohol, ammonia, alkali hydroxides, acetic anhydride and also in mixtures of two solvents. The brominating agents employed have been liquid bromine, bromine in acetic acid, bromine in aqueous potassium bromide, potassium bromide and potassium bromate. The iodinating agents employed have been iodine in aqueous potassium iodine, iodine in acetic acid and nitrogen iodide in ammonical solutions. Bromo- and iodo-derivatives of thymol have been obtained.



## 83. Halogenation, XIX. Bromination of Phenanthrene.

P. S. VARMA, Benares.

Bromination of phenanthrene has been carried out by the direct action of bromine in the presence of substances such as nitric acid, nitro-sulphonic acid, etc., which have not been tried before, in the dark, in diffused daylight and in direct sun-light at different temperatures. In some cases a very good yield of the bromo-derivatives, better than that obtained hitherto by other methods, has been obtained.

## 84. Halogenation, XX. Uranium oxide as a Halogen Carrier.

P. S. VARMA, Benares.

Experiments have been carried out on the halogenation of aromatic hydrocarbons and their mono substituted derivatives in the presence of uranium oxide. A good yield of the halogen derivatives has often been obtained. In some cases additive compounds and in others substitution derivatives have been isolated.

## 85. Finely divided Copper in the reaction of the Sulphur monochloride and Sulphur dichloride with Esters of aromatic Hydroxy acids.

N. W. HIRWE, G. V. JADHAV, and Y. M. CHAKRADEV,  
Bombay.

Neither sulphur monochloride nor sulphur dichloride reacts with methyl salicylate alone. On the addition of finely divided copper to the reaction mixture a solid is immediately obtained, which is Di (3-carbomethoxy-4-hydroxy phenyl) thio-ether.

The reaction takes place also in the presence of cuprous chloride.

## 86. Reaction of Thionyl Chloride with Esters of Aromatic Hydroxy acids in the presence of finely divided Copper. Part II.

N. W. HIRWE, G. V. JADHAV, and Y. M. CHAKRADEV,  
Bombay.

Methyl *o*-cresotinate and methyl *m*-cresotinate were heated with thionyl chloride in the presence of finely divided copper. A solid was obtained which proved to be a thio-ether. The acids were obtained on hydrolysis of the esters and their constitutions are described. Various salts and other derivatives such as acetoxy, benzoxyloxy, methoxy, etc. have also been studied.

## 87. Reaction of Thionyl Chloride with Esters of Aromatic Hydroxy acids in the presence of finely divided Copper. Part III.

N. W. HIRWE, G. V. JADHAV, and Y. M. CHAKRADEV,  
Bombay.

In extension of the reaction in Part II, methyl resorcyate was chosen. The reaction was so vigorous that no definite compound could be isolated. The reaction was moderated by converting the methyl resorcyate to 4-methoxy methyl salicylate and causing it to react with thionyl chloride in the presence of finely divided copper. A solid was obtained which was hydrolysed to an acid of which the constitution has been described.



Various salts and other derivatives such as acetoxy, benzoyloxy and methoxy are described.

*o*-Nitro phenol and esters of nitro salicylic acids do not yield the thio-ether under similar conditions. In general it may be stated that groups like OH, OCH<sub>3</sub> and CH<sub>3</sub> accelerate the reaction by their presence, while groups like NO<sub>2</sub> and COOH inhibit it.

#### 88. A New General Method for Synthesis of substituted *o*-Aldehydocarboxylic acids.

S. N. CHAKRAVARTI, Chidambaram.

The method consists in oxidising a symmetrically disubstituted or symmetrically tetra-substituted naphthalene derivative. The idea is that, whichever benzene nucleus is oxidised, the same phthalonic acid or acids should be obtained under the specified conditions. A number of such oxidations have been successfully tried. 5-Methoxy-phthalaldehydic acid, m.p. 144° has been prepared by oxidising 2:6-dimethoxy-naphthalene and also synthesised from known 5-Methoxy-phthalonic acid.

#### 89. The Rôle of finely divided Copper in the Action of Thionyl chloride on the Esters of Aromatic Hydroxy acids: The Mechanism of the Reaction.

N. W. HIRWE, G. V. JADHAV, and Y. M. CHAKRADEV, Bombay.

The mechanism of the reaction has been studied. First sulphur monochloride is obtained by the action of copper on thionyl chloride. Then sulphur dichloride is obtained by the action of cuprous chloride on thionyl chloride. Sulphur monochloride and dichloride act on methyl salicylate in the presence of copper or cuprous chloride to give a thio-ether. Copper chloride and sulphur dioxide interact regenerating cuprous chloride which keeps the reaction going.

#### 90. Bromination of Binuclear Compounds.

G. V. JADHAV and Y. I. RANGAWALA, Bombay.

Previous work has been extended to the esters of *p*-nitro and *m*-nitro benzoic acids, when mono and di-bromo compounds are obtained according to the conditions of the reactions. The first bromine atom always enters the nucleus which has no nitro group and in the position meta to the carbophenoxy group and the other bromine atom goes para to the first. The bromination of the phenyl and *o*-, *m*-, and *p*-cresyl esters has also been studied. The complete deactivation of the nucleus with nitro groups is interesting.

The position taken up by bromine atom is in accordance with the position taken by a nitro group in nitration. (*Neumann, Ber.*, 18, 3320; *ibid.*, 19, 2020 and 2980.)

#### 91. Nitration. Part VII. Nitration of *o*-Xylene.

P. S. VARMA, Benares.

Nitration of *o*-xylene has been carried out under different conditions using nitric acid alone or nitric acid in conjunction with plaster of Paris, acetic anhydride, sulphuric acid, and nitro-sulphonic acid. When nitric acid is used alone, some *o*-toluic acid is also formed. In the presence of other substances, however, only nitro-xylenes are obtained. The best yield of the mono-nitro-derivative has been obtained by using a mixture of fuming nitric and nitro-sulphonic acids.



## 92. Reduction of 2 : 4-Dinitrotoluene.

P. S. VARMA, Benares.

The reduction of 2 : 4-dinitrotoluene has not been systematically studied before. The authors have tried the reducing action of metallic sodium and methyl and ethyl alcohols, zinc dust and caustic soda, aluminium dust and caustic soda, stannous chloride in hydrochloric acid, tin and hydrochloric acid, zinc and hydrochloric acid, magnesium powder and ammonium chloride solution, zinc-copper couple, aluminium-mercury-couple, alcoholic solution of ammonium sulphide, as a result of which a number of reduction products, amongst which diaminotoluene, 4-nitro-2-aminotoluene, 2-nitro-4-amino-toluene, 2 : 2'-dimethyl-5 : 5'-dinitro-azoxy-benzene, 2 : 2'-dimethyl-5 : 5'-dinitro-azoxy-benzene and some other products such as 3 : 3'-dinitro-4 : 4'-ditolyl sulphide, 3-nitro-6-tolyl methyl or ethyl ether, have been obtained.

93. Steric Hindrance in Substituted Phthalic Acids. Part III. The  $\beta$ -monomethyl ester of 3-Nitro-phthalic acid.

P. RAMASWAMI AYYAR, Bangalore.

The structure of this substance (m.p. 163-164°) has been definitely established for the first time by the regulated heating of its silver salt. A quantitative yield of pure methyl *meta*-nitrobenzoate proves it to be the 1-ester of 3-nitro-phthalic acid.

## 94. Steric Hindrance in Substituted Phthalic Acids. Part IV. The isomeric Monomethyl Esters of 4-Nitrophthalic acid.

P. RAMASWAMI AYYAR and V. N. PAI, Bangalore.

Pure specimens of two isomeric esters (m.p. 132° and 144°) have been prepared by half-saponification of the pure dimethyl ester as well as by half-esterification of the pure 4-nitro-phthalic acid. The regulated heating of their silver salts respectively yielded pure *para* and *meta*-nitro-benzoic esters, establishing their structures definitely as the 1-ester and 2-ester of 4-nitro-phthalic acid respectively.

## 95. Condensation of Ethylene Chlorhydrin with Resorcinol and Derivatives of the Products.

D. C. MOTWANI and T. S. WHEELER, Bombay.

2-Hydroxy-4 ( $\beta$ -hydroxy)-ethoxychalkone prepared from 2-hydroxy 4 ( $\beta$ -hydroxy)-ethoxyacetophenone (I) and benzaldehyde gave two acetyl derivatives, viz. 2-hydroxy-4 ( $\beta$ -acetoxy)-ethoxychalkone (violet ferric chloride reaction) and 2-acetoxy-4 ( $\beta$ -acetoxy)-ethoxychalkone. The latter was converted into the corresponding flavone *via* the dibromide, which on de-ethylation furnished 7-hydroxyflavone. Alcoholic sulphuric acid converted the chalkone into 7-( $\beta$ -hydroxy)-ethoxyflavanone.

5-bromo-6 ( $\beta$ -hydroxy)-ethoxybenzylidenecoumaranone was prepared from the dibromide of the chalkone.

2-hydroxy-4 ( $\beta$ -hydroxy)-ethoxy-4-methoxychalkone similarly prepared gave also a *mono* (characterized by violet ferric chloride reaction) and a *diacetyl* derivative. The dibromide of the latter can be hydrolyzed to 7- $\beta$ -hydroxy-ethoxy-4'-methoxyflavone. The chalkone of (I) with salicylaldehyde was converted into the pyrrilium salt and then into a ferri-chloride, perchlorate, picrate, and mercurichloride. (I) also condensed with *o*-nitro-benzaldehyde. (I) gave a diacetyl derivative, which on reduction with zinc amalgam gave 2-hydroxy-4-( $\beta$ -hydroxy)-ethoxy ethyl benzene.



The following are prepared :—acetyl, benzoyl, chloro-derivatives of *m*-methoxy ( $\beta$ -hydroxy)-ethoxy phenylene.

Ethyl resorcinol gave with ethylene chlorohydrin (i) 2-hydroxy-4 ( $\beta$ -hydroxy)-ethoxy ethyl benzene and (ii) 2:4-di ( $\beta$ -hydroxy) ethoxy ethyl benzene, identical with the reduction products of the corresponding ethoxy derivatives of resacetophenone.

#### 96. C-Alkyl Resorcinols. Part II. Synthesis of Poly-Alkyl Resorcinols.

R. C. SHAH and P. R. MEHTA, Bombay.

A number of polyalkyl-resorcinols have been synthesised with a view to studying the influence of two or more alkyl groups in the resorcinol nucleus on the phenol coefficient.

Resacetophenone by nuclear methylation gave 4-methoxy-3-methyl-2-hydroxy-acetophenone, which, on reduction with zinc amalgam and hydrochloric acid, gave 2-hydroxy-3-methyl-4-methoxy-ethyl benzene. Demethylation of the last compound by hydriodic acid gives 2-methyl-4-ethyl-resorcinol.

4-ethyl-resorcinol obtained by the Clemmensen reduction of resacetophenone gave, by the Hoesch reaction, 5-ethyl-2:4-dihydroxy-acetophenone. This on reduction afforded the required 4:6-diethyl-resorcinol.

#### 97. C-Alkyl Resorcinols. Part III. Derivatives of 4-ethyl-resorcinol.

R. C. SHAH and B. V. SAMANT, Bombay.

The reactions of 4-ethyl-resorcinol are being investigated, with particular reference to preparation of compounds of possible therapeutic value. In addition to many of its simple derivatives, which have been prepared for the first time, a number of interesting compounds like coumarins, the corresponding fluorescein and its dibromo derivative, pyryllium salts, and their colour bases which are soluble in chloroform, have been obtained from 4-ethyl resorcinol or its aldehyde, obtained from it by Adam's zinc cyanide method.

Condensation with formaldehyde in acidic solution gives the methylene compound from which further derivatives have been obtained by acetylation and bromination. Some of these compounds are expected to be of interest from the point of view of their antiseptic property.

#### 98. A Synthesis of 5:6-Dimethoxyhomophthalic acid and of some Mono-methoxyhomophthalic acids.

S. N. CHAKRAVARTI and M. SWAMINATHAN, Chidambaram.

2-Carboxy-5:6-dimethoxy-phenylacetonitrile (m.p. 175°) prepared from 4:5-dimethoxy-hydrindone *via* the *iso*-nitroso compound, was hydrolysed to the corresponding acid (m.p. 192°). Similarly, 5-methoxy-hydrindone gave an *iso*-nitroso ketone (m.p. 221°) and a corresponding nitrile (m.p. 177°). On hydrolysis, the latter furnished an acid (m.p. 222°) and the *iso*-nitroso compound gave a diketohydrindone (m.p. 152°; related quinoxaline, m.p. 140°). In nitrobenzene solution 6-methoxy-hydrindone (m.p. 109°) is formed in 20% yield by the ring closure of *p*-methoxy-cinnamoyl chloride with aluminium chloride (*cf.*, Perkin and Robinson who record failure). 4-Methoxy-2-carboxy phenyl acetonitrile (m.p. 140°) was prepared from its *iso*-nitroso derivative (m.p. 234°) which, on hydrolysis, gave the acid (m.p. 188°). 6-Methoxy-1:2-diketohydrindone had m.p. 126° (its quinoxaline, m.p. 156°). Yields obtained in the above reactions averaged over 85%.



99. Chemistry of Imido Chlorides. Part V. Action of Benzanilide-imido-chloride on Phenols in the presence of Aluminium chloride.

R. C. SHAH, Bombay.

It is well known that benzanilide-imido-chloride reacts with sodium derivatives of phenols to give imino ethers.

It is now found that benzanilide-imido-chloride reacts smoothly with resorcinol and orcinol in presence of anhydrous aluminium chloride giving anils of 2:4-dihydroxy-benzophenone and 2:4-dihydroxy-6-methyl-benzophenone, which are isolated in good yields as the sparingly soluble hydrochlorides. The anils on hydrolysis give the corresponding hydroxy-benzophenones.

$\alpha$ - and  $\beta$ -Naphthols react similarly giving the corresponding anils from which the ketones are obtained on hydrolysis with dilute sulphuric acid.

Phloroglucinol also condenses smoothly, but appears to give the dianil of 2:4-dibenzoyl-phloroglucinol, which on heating with water in a sealed tube gives the free ketone.

100. Synthesis of Chloral-salicylamide and related products.

N. W. HIRWE, Bombay.

Chloral is condensed directly with (a) salicylamide and (b) *o*-methoxy benzamide by heating the mixture on the water-bath. Chloral salicylamide and *o*-methoxy benzamide are obtained. These are further reduced with glacial acetic acid and zinc dust.

The compounds are prepared in order to study the hypnotic properties of the chloral group in conjunction with the antiseptic properties of salicylic acid. The chemo-therapeutic index is under investigation.

101. The Condensation of Benzotrichloride with deactivated Aromatic Nuclei.

A. P. KHANOLKAR, P. S. REGE, and T. S. WHEELER, Bombay.

It is known that benzotrichloride readily condenses with phenol and aniline. The reaction is vigorous and difficult to control. It has now been found that if the phenyl nucleus is deactivated by the attachment of groups which act as electron sinks, smooth reaction with the elimination of hydrogen chloride is obtained. Thus acetanilide and formanilide react smoothly; acetanilide gives a compound (m.p. 160°) and a base (m.p. 132°); dihydrochloride (m.p. 222°), benzoyl derivatives (m.p. 163° and 117°). Nitranilines and chloranilines also react smoothly.

The hydroxy-benzoic and naphthoic acids also condense. Thus *m*-hydroxy benzoic acid gives a compound (m.p. 125°) which slowly dissolves in hot alkali and on treatment with mineral acids precipitates a mixture of acids. These acids readily give benzoyl derivatives. Camphoric acid also reacts smoothly. Somewhat surprisingly when benzotrichloride is heated with concentrated formic acid, rapid and smooth hydrolysis to benzoic acid takes place.

102. The Nidhone Process for the Synthesis of 2-Acyl-resorcins. Part II. 2-Acetyl-resorcin.

D. B. LIMAYE and D. D. GANGAL, Poona.

In Part I, 2-benzoyl resorcin has been synthesized from resorcin by a set of operations, designated as 'The Nidhone Process'.



The preparation of 2-acetyl-resorcin from acetyl 4-methyl-umbelliferone (m.p.  $168^{\circ}$ ), fixes the position of the entering acetyl group in 4-methyl-umbelliferone as 8.

The 2-acetyl resorcin is characterised by the formation of a dibenzoyl derivative (m.p.  $106^{\circ}$ ) and a dimethyl ether (m.p.  $73^{\circ}$ ), which on oxidation gives successively 2:6-dimethoxy-phenylglyoxylic acid (m.p.  $93^{\circ}$ ), and 2:6-dimethoxy-benzoic acid, a known compound. The dimethyl ether gives a semicarbazone (m.p.  $220^{\circ}$ ) and a phenylhydrazone (m.p.  $153^{\circ}$ ).

Condensation of 2-acetyl-resorcin with acetoacetic ester regenerates the 8-acetyl-4-methyl-umbelliferone.

### 103. Reactivity of Dimethyldihydroresorcin. Part IV. Compounds with Tetrazonium chlorides.

B. H. IYER and G. C. CHAKRAVARTI, Bangalore.

The azo- and oxyazo-compounds obtained by coupling dimethyldihydroresorcin with diazotized mono-amines, proved to be valuable dyes for wool and silk.

With a view to preparing dyes substantive to cotton, dimethyldihydroresorcin has now been coupled with tetrazotized benzidine and *ortho*-tolidine and diazotised *p*-nitraniline. The azo- and oxyazo-compounds thus obtained are described. The mechanism of the reaction is also discussed.

### 104. Condensation of Acetoacetic ester with Phenolic ethers.

G. R. GOGTE, Bangalore.

The work of Limaye, Gogte, Bhawe, and Dixit has shown that ethyl acetone-dicarboxylate reacts with phenolic ethers to yield  $\beta$ -substituted phenylglutaconic acids. The reaction with anisole and acetoacetic ester, in place of acetone-dicarboxylic ester, however, gives a monobasic acid (m.p.  $162^{\circ}$ , M.W., 300, empirical formula  $C_{18}H_{20}O_4$ ), and appears to have arisen out of two molecules of anisole and one of acetoacetic ester. *o*-Cresol methyl ether, also gives a similar product with acetoacetic ester; in the case of *p*- and *m*-cresol methyl ethers, the corresponding 4-methyl-coumarins are obtained.

### 105. Perkin's Reaction with Glutaconic Anhydrides.

G. R. GOGTE, Bangalore.

In a paper by Limaye, Gogte, and Bhawe (in the press) it has been shown that the action of sodium acetate and acetic anhydride on the anhydrides of  $\beta$ -aryl-glutaconic acids, proceeds according to Perkin's reaction, the reaction products being named glutaconyl acetic acids. This structure receives support from the products obtained by their successive hydrolysis with alkali.

In the case of the anhydride of the glutaconic acid from *p*-cresol methyl ether, however, if the reaction is carried out under different conditions, a product is obtained (m.p.  $168^{\circ}$ ) which is quite stable towards alkalis, while the product obtained under normal conditions melts at  $129^{\circ}$ . This new product is a monobasic acid (M.W., 316, empirical formula,  $C_{17}H_{16}O_6$ ). This new reaction appears to be of general application with  $\beta$ -aryl glutaconic acids of the *ortho* series.



## 106. Condensation of Glyceryl Chlorhydrin with Resacetophenone and the Study of the products obtained.

D. R. NADKARNI, Bombay.

With a view to prepare products which may serve as basic substances for the synthesis of flavones and their derivatives, resacetophenone has been condensed with glyceryl chlorhydrin in the presence of 40% potassium hydroxide. The resulting mono-ether (m.p.  $160^{\circ}$ ), gives a colouration with ferric chloride, so that it seems that the hydroxyl group in the ortho position to the acetyl group remains intact. The ether gives a tri-acetyl derivative and condenses with benzaldehyde in the presence of alcoholic potash to yield the corresponding *chalkone* (m.p.  $200^{\circ}$ ).

## 107. A Synthesis of Brazilinic acid.

J. N. RÂY, P. R. WADHA, and S. S. SILOOJA, Lahore.

The Perkin-Robinson synthesis suffers from the disadvantage that the steps are not unambiguous. In view of the fact that the accepted structure of brazilin is based on the constitution of brazilinic acid, an alternative synthesis has been offered.

The authors have converted 4':4:5-trimethoxy-2-hydroxy-benzophenone into the 2-nitro-derivative by nitration. Reduction, replacement of the amino group by a cyano group and subsequent hydrolysis gives the 2-carboxylic acid, which when caused to react with sodium chloroacetate in alkaline solution, yields brazilinic acid identical with the natural product.

## 108. Derivatives of 1-Hydroxy-2-naphthoic acid.

G. V. JADHAV and S. N. RAO, Bombay.

The nitration of 1-hydroxy-2-naphthoic acid gives a 3:4-dinitro-hydroxy acid or 1:3:4-trinitro-naphthoic acid, depending on the concentration of the acid used. The constitution of these have been determined.

1-Hydroxy-3:4-dinitro-2-naphthoic acid gave a substance  $C_{21}H_8O_{10}N_4$  by decarboxylation and loss of two molecules of water when acetylation, benzoylation or esterification were attempted. The salts of this acid are described.

The sulphonic group of 1-hydroxy-4-sulpho-2-naphthoic acid was replaced by chlorine or bromine. The salts of the resulting acid are described.

## 109. Synthesis of Ethyl 2:3-diketo-1:4-endothiocyclohexane-1:4-dicarboxylate.

R. C. DAS GUPTA and P. C. GUHA, Bangalore.

The general applicability of the method described in the foregoing paper has been established by the synthesis of ethyl 2:3-diketo-1:4-endothiocyclohexane-1:4-dicarboxylate from the disodium derivative of oxalyl thiodiglycollic ester with ethylene bromide. It is expected that replacement of the carbethoxy groups by hydrogen and the reduction of the carbonyl groups to methylene will lead to the formation of 1:4-endothiocyclohexane.

## 110. Studies in Bridge Formation.

D. R. MEHTA and P. C. GUHA, Bangalore.

Methylene iodide, on interaction with the disodio derivative of Schiebel and Missel's ester, gave a *bis* methylene derivative instead of



the expected bridge compound, because, on hydrolysis, methylene-*bis*-dimethyldihydroresorcin (*cf. Annalen*, 294, 316) was produced. Therefore, the compound described as ketonopinone (*Current Science*, 1933, August, 53) is methylene-*bis*-dimethyldihydroresorcin.

### 111. Synthesis of Norpinic acid.

K. N. GAIND and P. C. GUHA, Bangalore.

As an alternative to Kerr's complicated synthesis of norpinic acid, the following simple process has been evolved.

The tetracarboxylic ester obtained by condensing methylene iodide and chloracetol respectively with the disodium derivative of *isopropylidene* dimalonic ester and methylenedimalonic ester, has yielded norpinic acid on hydrolysis and decarboxylation. The method for the preparation of *isopropylidene* malonic and dimalonic esters has been improved.

### 112. Studies in Bridge Formation.

K. N. GAIND and P. C. GUHA, Bangalore.

Ethyl succino-succinate has yielded interesting bridged compounds with methylene iodide, chloracetol, iodine and carbonyl bromide, the first, second, and fourth compound having the bridge through CH<sub>2</sub>, C-Me, and CO. With iodine, a substance with a direct para linkage has been formed. The bridged structure follows from molecular weight determination and elementary analysis.

### 113. Studies in Bridge Formation. Synthesis of Ketonorpinic acid and Ketoapo-pinanedicarboxylic ester.

R. C. DAS GUPTA and P. C. GUHA, Bangalore.

'Gaureschi' imide reacts with carboxyl bromide to yield  $\alpha:\alpha$ -dicyanoketonorpinimide (I). Five compounds viz. 1:3-dicyano-2:2-dimethyl-1-carbamylcyclobutane-4-one-3-carboxylic acid, 1:1:3-tricyano-2:2-dimethylcyclobutane-4-one,  $\alpha$ -carbamyl- $\beta:\beta$ -dimethyl glutaronitrile,  $\alpha$ -cyano- $\beta:\beta$ -dimethyl glutarimide,  $\alpha$ -carbamyl- $\beta:\beta$ -dimethyl glutarimide, constitute an interesting series of degradation products of  $\alpha:\alpha$ -dicyanoketonorpinimide in the process of its final conversion into  $\beta:\beta$ -dimethyl glutaric acid by hydrolysis. Compound (I) yields with sulphuric acid at 105° and 130° respectively the *cis* (II) and the *trans* ketonorpinic acids (III).

The disodium derivative of ethyl acetonedicarboxylate reacting with chloracetol in benzene suspension and at high temperatures yields ethyl ketonorpinate (IV) which is hydrolysed by baryta to the *cis* acid (II).

A new method has been devised for the synthesis of 1:3-bridged *cyclo*-hexane compounds. The disodium derivative of (IV), reacting with trimethylene bromide, has yielded ethyl ketoapopinane dicarboxylate.

### 114. Chemistry of Imido-chlorides. Part IV. Condensation of Benzanilideimido-chloride with urethanes: A New Synthesis of 2-phenyl-4-oxy-quinazolines.

R. C. SHAH and M. B. ICHAPORIA, Bombay.

The sodium derivatives of urethane and substituted urethanes condense with imido-chlorides derived from acylamines in suspension in ether. Phenyliminobenzyl urethane, an oil, formed from benzanilide-iminochloride and urethane, gives high melting products with hydrazine, phenylhydrazine, etc. which serve for its characterisation. The action of heat converts it into 2-phenyl-4-oxy-quinazoline of settled constitution,



Similarly methyl and acetyl urethane furnish the corresponding quinazolines.

Benz- $\alpha$ - and  $\beta$ -naphthanilido imidochlorides condense with ethyl urethane giving  $\alpha$ - and  $\beta$ -naphthyl iminobenzyl urethanes which are transformed by heat into 2-phenyl-7:8-benz-quinazoline (m.p. above  $300^{\circ}$ ) and 2-phenyl-5:6-benz-quinazoline (m.p.  $295^{\circ}$ – $298^{\circ}$ ).

115. The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part V. The Benzoxazole System.

R. D. DESAI, R. F. HUNTER and A. R. K. KHALIDI,  
Aligarh.

It has been found in accordance with the views expressed in earlier parts of this series (Hunter, *J. Chem. Soc.*, 1930, 125 and later) that the benzoxazole system exhibits the greatest similarity to the benzthiazole system (Hunter, *J. Chem. Soc.*, 1926, 1385 and later) as regards the tautomeric mobility and behaviour on bromination of the 1-amino, 1-anilino, 1-hydroxy, and 1-thiol derivatives.

116. The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part VI. The  $\beta$ -Naphthathiazole System.

R. D. DESAI, R. F. HUNTER and M. A. KUREISHY, Aligarh.

The  $\beta$ -naphthathiazole system behaves analogously to the  $\alpha$ -naphthathiazole system studied by Hunter and Jones (*J. Chem. Soc.*, 1930, 941); the heterocyclic ring exhibiting strikingly aromatic characteristics in the mobile derivatives.

117. The Formation and Stability of Polybromide Derivatives of Heterocyclic Compounds. Part IV. 5-Methyl and 5:5-Dimethyl- $\psi$ -thiohydantoins.

BASHIR AHMAD, R. D. DESAI and R. F. HUNTER, Aligarh.

The  $\psi$ -thiohydantoins examined by Farooq and Hunter (*J. Indian Chem. Soc.*, 1932, 9, 545) contain two potentially mobile hydrogen atoms belonging to the keto-enol complex, and the effect of replacement of these by methyl groups on the behaviour of certain  $\psi$ -thiohydantoins towards bromine in inert solvents has been examined. The experiments recorded in this paper indicate that the effect of the keto-enol system is negligible as far as perbromide to bromo-substitution hydroperbromide transformations are concerned.

118. The Directive Effect of Substituents on the Cyclisation of Substituted *s*-Diarylthiocarbamides. Part IV. *p*'-Substituted-*p*-cyano-*s*-diphenylthiocarbamides.

M. OMAR FAROOQ and R. F. HUNTER, Aligarh.

In all the cases examined ( $R=Me, I, Br, Cl, F$ ), cyclisation takes place on the nucleus opposite to the point where the *meta* directive cyano group is situated. This is in accordance with the general view that *meta* substitution is essentially a residual effect produced by the disappearance of free affinity from the *o-p*-positions in an aromatic nucleus.



## 119. Studies in Heterocyclic Compounds. Part III.

A. C. SIRCAR and S. C. SEN, Calcutta.

This continues the work of Sircar and De (*J. Indian Chem. Soc.*, 1926, 3, 312) and Sircar and Pal (*ibid.*, 1932, 9, 527) and was undertaken with the object of studying how the reactivity of the aminohydroxy groups in ortho-amino phenol is influenced by the introduction of a compact heterocyclic nucleus in its molecule and also how, in compounds containing two dissimilar heterocyclic rings in their molecules, the properties of the different heterocyclic nuclei are affected by each other. 2-Hydroxy-3-amino-phenazine (Ullmann and Mauthner, *Ber.*, 35, 4308) was chosen as the starting material and attempts have been made to introduce various types of new heterocyclic rings *via* the amino hydroxy groups situated in the ortho position. It has now been found that, unlike *o*-amino phenol, 2-hydroxy-3-aminophenazine is not so well adapted for the formation of heterocyclic compounds. Evidently the already existing azine ring in the molecule of 2-hydroxy-3-aminophenazine strongly militates against the otherwise easy reactivity of the *o*-amino hydroxy group.

## 120. A Synthesis of 4-Hydroxy-quinoline-3-carboxylic acid.

R. C. SHAH and V. R. HEERAMANER, Bombay.

In continuation of previous work the authors have now synthesised 4-hydroxy-quinoline-3-carboxylic acid (m.p. 258–260°) by the condensation of formanilide and malonic ester in the presence of phosphorus oxychloride. Camps (*Ber.*, 1901, 34, 2703) gives m.p. 261–263°.

## 121. A Synthesis of 2:3-Methylene-dioxy-11:12-dimethoxy-oxy-protoberberine, an isomer of oxyberberine.

S. N. CHAKRAVARTI and M. SWAMINATHAN, Chidambaram.

N- $\beta$ -Piperonyl-ethyl-5:6-dimethoxy-homophthalimide, (m.p. 223°) obtained by condensing  $\beta$ -piperonylethylamine and 5:6-dimethoxy homophthalic acid, was hydrolysed to N- $\beta$ -piperonyl-ethyl-5:6-dimethoxy-homophthalamic acid (m.p. 245°). The latter was converted into the methyl ester (m.p. 169–170°). The latter, on treatment with phosphorous oxychloride gave 2:3-methylene-dioxy-11:12-dimethoxy-oxy-protoberberine (m.p. 230–231°).

122. Preliminary Synthetic Experiments in the Cytisine group.  
Part I. Attempted Synthesis of Ewin's structure for Cytisine.

S. N. CHAKRAVARTI and A. VENKATASUBBAN, Chidambaram.

Five unsuccessful methods were made to synthesise cytisine according to Ewin's formulæ. The following results were obtained:—

(i) Nitration of 3-methyl-cinnamic acid was shown to give 2-nitro-3-methyl-cinnamic acid (m.p. 244°), 4-nitro-3-methyl-cinnamic acid (m.p. 251°), and 6-nitro-3-methyl-cinnamic acid (m.p. 224°);

(ii) Oxy-uvitic aldehyde was converted into a mono-Schiff's base (m.p. 161°) and then into 3-methyl-5-aldehyde-6-hydroxy-cinnamic acid (m.p. 212°), which was converted into the ester (m.p. 129°), and then into the hydrazide;

(iii) Attempts were made to effect the internal condensation of 6:8-dimethyl-1:2:3:4-tetrahydro-N-nitroso-quinoline between the 8-methyl and nitroso groups;



(iv) 8-cyano-6-methyl-quinoline (m.p.  $90^{\circ}$ ), 6-methyl-quinoline-8-carboxylic acid (m.p.  $169^{\circ}$ ), 6-methyl-1:2:3:4-tetrahydroquinoline-8-carboxylic acid (m.p.  $190-191^{\circ}$ ), 6-methyl-N-nitroso-tetrahydroquinoline-8-carboxylic acid (m.p.  $138^{\circ}$ ) were prepared.

Attempts to convert  $\omega$ - $\omega$ -dibromomesitylene to the corresponding dialdehyde were unsuccessful.

123. A Synthesis of 2:3-Methylene-dioxy-11:12-dimethoxy-tetrahydro-protoberberine, an Isomer of Tetrahydro-protoberberine, and a Synthesis of 2:3:11:12-tetramethoxy-tetrahydroprotoberberine, an Isomer of Tetrahydro-palmatine.

S. N. CHAKRAVARTI and M. SWAMINATHAN, Chidambaram.

2:3-Dimethoxy-phenylacetic acid, prepared by an improved method, was condensed with  $\beta$ -piperonylethylamine to 2:3-dimethoxy-phenyl-aceto- $\beta$ -piperonylethylamide (m.p.  $108^{\circ}$ ). The amide was cyclised to 6:7-methylene-dioxy-1 (2':3' dimethoxy-benzyl)-dihydro-*iso*quinoline and then reduced to tetrahydro-*iso*quinoline hydrochloride (m.p.  $160^{\circ}$ ). The formyl derivative of 6:7-methylenedioxy-1 (2':3' dimethoxy-benzyl)-1:2:3:4-tetrahydro *iso*quinoline was converted into 2:3-methylene dioxy-11:12-dimethoxy-tetrahydro protoberberine, and the latter reduced to 2:3-methylene dioxy-11:12-dimethoxy-tetrahydroprotoberberine (m.p.  $127^{\circ}$ ). The corresponding protoberberinium iodide (m.p.  $252^{\circ}$ ), chloride (m.p.  $220^{\circ}$ ), and 2:3-methylene dioxy-11:12-dimethoxy-oxy-protoberberine (m.p.  $231^{\circ}$ ) were also prepared.

Next 2:3-dimethoxy-phenyl-aceto- $\beta$ -veratrylethylamide (m.p.  $131^{\circ}$ ) was prepared by condensing  $\beta$ -veratryl-ethylamine with 2:3-dimethoxy-phenylacetic acid, and converted first into the dihydro-*iso*quinoline and then into 6:7-dimethoxy-1 (2':3'-dimethoxy-benzyl)-1:2:3:4-tetrahydro-*iso*quinoline (hydrochloride, m.p.  $204^{\circ}$ ). The formyl derivative of the last base was converted into 2:3:11:12-tetramethoxy-tetrahydroprotoberberine (m.p.  $163^{\circ}$ ), through the dihydroprotoberberine.

124. Experiments on the Synthesis of Pyrrolo-indolines.

J. N. RÂY and S. SILOOJA, Lahore.

The structure of eserine advanced by Barger has received confirmation from the researches of Robinson and collaborators. In the present paper a pyrroloindolenine with the requisite quaternary carbon atom has been synthesised from lævulinic acid. The cyanhydrin of the latter on hydrolysis furnishes a lactonic acid which has been converted *via* its chloride into an anilide. This, on treatment with hydrazine, is transformed into a hydrazide which in turn changes into an azide by nitrous acid. Thermal decomposition of the latter gives a carbimide which furnishes a triacetyl derivative. Ring closure followed by hydrolysis gives noreserimethole which has been isolated as its picrate.

125. Studies in the Derivatives of Pyrazolone. Condensation of the Hydrazine salicylic acids with Ethyl aceto-acetate.

N. W. HIRWE and B. V. PATIL, Bombay.

With a view to study new antipyretic compounds, it was sought to condense the hydrazino salicylic acids with ethyl aceto-acetate.

3-Hydrazino hydrochloride of salicylic acid was condensed with ethyl aceto-acetate. A solid is obtained with a high melting point.



5-Hydrazino hydrochloride of salicylic acid was similarly condensed. The condensation compound on treatment with glacial acetic acid gives an acetyl derivative.

The hydrazines were prepared from the corresponding nitro acids by reduction, diazotisation and further reduction.

## 126. Quinoline Derivatives. Part II. Pyrazolo-quinolines.

J. N. RÂY and K. S. NARANG, Lahore.

Phenyl methyl pyrazolone condenses with *o*-nitro aromatic aldehydes to give the corresponding arylidene derivatives. These on reduction furnish, in the case of *o*-nitro benzaldehyde, a quinoline with a hydroxyl group attached to the ring nitrogen and, in the case of nitro-veratric aldehyde, a quinoline and, in the case of nitro-piperonal, an open chain aromatic amine. The latter can be converted into a quinoline by simple heating at its melting point. The structure of these products has been determined by a comparison of their absorption spectra at equivalent dilution in different solvents.

## 127. Extension of Michael's Reaction. Part IV.

T. N. GHOSH and P. C. GUHA, Bangalore.

Ethyl acetonedicarboxylate reacts with thiocarbimides to give ethyl 2-arylimino-thiopyran-4:6-dione-3-carboxylate. This compound reacts with benzaldehyde to give a bridged thiopyran compound. Ethyl acetonedicarboxylate reacts with phenylisocyanate to give ethyl  $\alpha:\alpha'$ -phenyl-carbamyl-acetonedicarboxylate, which reacts with aldehydes to give, with the elimination of a molecule of water and two molecules of alcohol, a tricyclic compound.

Ethyl methylenedimalonate reacts with phenylisocyanate to give  $\alpha$ -phenylcarbamido- $\alpha:\alpha':\alpha'$ -tricarbethoxy-N-phenyl-glutarimide. The condensation of various dienes with phenylisocyanate, carbethoxythiocarbimides are being studied.

## 128. Extension of Michael's Reaction. Part V.

T. N. GHOSH and P. C. GUHA, Bangalore.

The work reported before (1932) has now been extended. Phenyl azocarboxylic ester reacts with the sodium derivatives of ethyl acetoacetate, cyanacetate and acetyl acetone to yield  $\beta$ -N-carbethoxyacetyl-methyl- $\beta$ -phenyl carbazinic ester,  $\beta$ -N-carbethoxycyanomethyl- $\beta$ -phenyl-carbazinic ester and  $\beta$ -N-diacetylmethyl-N-phenylcarbazinic ester respectively. Ethyl azodicarboxylate with sodium acetoacetic ester gives  $\text{CO}_2\text{Et}\cdot\text{N}(\text{CHAc}\cdot\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ . The addition compound  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{NPh}\cdot\text{N}(\text{Na})\cdot\text{CO}_2\text{Et}$  obtained from sodium urethane and phenylazocarboxylic ester is hydrolysed in the presence of acids into urethane and  $\beta$ -N-hydroxy- $\beta$ -phenylcarbazinic ester which, on treatment with alkali, undergoes ring-closure and gives the potassium salt from which acids liberate the free hydroxy compound. The methyl and ethyl derivatives obtained from the potassium salt by the action of methyl and ethyl iodide respectively are different from the methyl and ethyl esters of phenylcarbazinic acid.

The additive compounds from mesoxalic ester phenylhydrazone  $\text{PhNH}\cdot\text{N}=\text{C}(\text{CO}_2\text{Et})_2$  with the sodium derivative of acetoacetic, cyanacetic or malonic ester are easily hydrolysed into  $\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}_2\text{H}$  which gives an azo compound on oxidation, and phenylhydrazine acetic acid on hydrolysis with alcoholic potash.



## 129. Formation of Heterocyclic Compounds.

T. N. GHOSH, Bangalore.

By condensing some carbamic acid derivatives with aniline, phenylhydrazine and thiosemicarbazides, some interesting heterocyclic compounds have been synthesized.

## 130. Alkaloido-cyclic-ureides. Part I.

P. NEOGY and A. K. SEN-GUPTA, Calcutta.

Owing to the presence of imido-hydrogen in proximity with carbonyl groups, alloxan and other cyclic ureides have acidic reactions and would, therefore, be capable of combination with alkaloids. The preparation, properties, rotation and probable constitution of compounds of alkaloids such as quinine, strychnine, etc. with alloxan are described.

## 131. Studies in Indigoid Dyes. Part IV. 2:1-Naphthathiophene-phenanthrene-indigos.

P. C. DUTTA, Muzaffarpur.

In continuation of the work of the present author on thionaphthene-phenanthrene-indigos described in Part I (*J. Indian Chem. Soc.*, 1932, 9, 99) and 1:2-naphthathiophene-phenanthrene-indigos in Part II (in the press), the present investigation was undertaken with a view to study the effect of the position of sulphur in the naphthalene ring on the colour of the naphthathiophene-phenanthrene-indigos. It deals with indigoid dyes obtained by condensing 2:1-naphthoxythiophene with phenanthraquinone and its various derivatives. The condensation was mostly brought about by conc. hydrochloric acid in glacial acetic acid solution of the constituents. The compounds described are generally deeper in shade than the corresponding isomeric 1:2-naphthathiophene-phenanthrene-indigos. They dissolve in hydrosulphite vat with a yellow or yellowish brown colour from which the original dyes are precipitated by oxidation with air. They are sparingly soluble in organic solvents.

## 132. Dyes derived from Acenaphthenequinone. Part IV. Indigoid Vat Dyes.

S. K. GUHA, Patna.

In continuation of the work of vat dyes reported in Part III of this series (Guha, *J. Indian. Chem. Soc.*, 1932, 9, 423), this paper describes the preparation and properties of a few more such compounds obtained by the condensation of acenaphthenequinone, its chloro, bromo, and methoxy derivative only with 5-methyl-3-hydroxy-thionaphthene (Auwers and Arndt., *Ber.*, 1909, 42, 541). The beautiful deep scarlet-red shades developed on cotton from an alkaline hydrosulphite vat and on wool from an acid bath from the first three substances are distinctly deeper than those obtained from Ciba Scarlet G and its halogen derivatives (Guha, *loc. cit.*). This result points to the conclusion that the introduction of a methyl-group in the 5-position of the thionaphthene nucleus in Ciba Scarlet G and its halogen derivatives deepens the shade of the colour of the substances.

## 133. Studies in Indigoid Dyes. Part V.

P. C. DUTTA, Muzaffarpur.

The present communication deals with indigoid dyes obtained by condensing 2:1-naphthoxythiophene with isatin and some of its deriva-



tives, acenaphthenequinone, 5-nitroacenaphthenequinone, 5:6-dinitro-acenaphthenequinone, aceanthraquinone and glyoxal and is a continuation of the work described in Part III on idigoid dyes to be published shortly. As expected, the compounds in this series are all brilliantly coloured glistening needles which impart a deep shade on cotton from hydrosulphite vat. On comparison of the colour produced on cotton by these dyes with the isomeric 1:2-compounds described in Part III (*loc. cit.*) it has been found that these 2:1-compounds produce colour generally towards red and although a deep shade is produced the colour effect is slightly lighter although in the phenanthrene series an opposite effect is noticed.

#### 134. Dyes derived from Acenaphthenequinone and Isatin.

P. C. DUTTA and DAMODAR PRASAD, Muzaffarpur.

The reaction of 6-chloro-3:4-tolylenediamine (Morgan and Drew, *J.C.S.*, 1920, 117, 784) on ortho-diketones has been further extended and the present communication deals with compounds produced by condensing 6-chloro-3:4-tolylenediamine with isatin, acenaphthenequinone and their various derivatives. The chloro-azines thus obtained were subjected to Ullmann's reaction and the corresponding aniline compounds obtained. As in the phenanthrene series the colour changes from yellow or brown to black with the introduction of the aniline group for the chlorine atom.

#### 135. The Effect of Substituent Groups on the Coupling of a Diazonium compound.

N. W. HIRWE and MISS K. D. GAVANKER, Bombay.

3-Diazo-salicylic acid was chosen to study the above effects and was coupled in alkaline solution with (1) phenol, (2) *o*-cresol, (3) *m*-cresol, (4) *p*-cresol, (5) *o*-nitro phenol, and (6) salicylic acid. It was found that, in the first four cases, the new compounds could be obtained, but in the case of the last two no compound could be isolated. This shows that the presence of OH or OCH<sub>3</sub> groups accelerate the coupling, while the presence of the NO<sub>2</sub> or COOH groups inhibits it.

#### 136. Dyes Derived from Isatin.

S. K. GUHA and H. P. BASU MALLICK, Patna.

5-Methyl-3-hydroxy-thionaphthene (Auwers and Arndt., *Ber.*, 1909, 42, 541) condenses with isatin and its various derivatives with the greatest ease. The condensed products come out rapidly and quantitatively on warming the constituents in glacial acetic acid solution in the presence of a little strong hydrochloric acid. The compounds obtained are,—3-indole-, 3(5-chloro)-indole-, 3(5-bromo)-indole-, 3(5-iodo)-indole-, 3(5:7-dibromo)-indole-, 3(5-bromo-7-nitro)-indole-, 3(5:7-dinitro)-indole-2' (5'-methyl)-thionaphthene-indigo.

#### 137. Dyes Derived from Phenanthraquinone.

P. C. DUTTA and DAMODAR PRASAD, Muzaffarpur.

The authors have succeeded in replacing the chlorine atom in 3-chloro-2-methyl-benzophenanthrene by the anilido group by Ullmann's reaction. The azine dyes, obtained by the condensation of 6-chloro-3:4 tolylenediamine with various phenanthraquinone derivatives, gave anilido compounds from which it has been found that the anilido group tends to change the colour of the products from yellow or brown to black.



138. Studies on the Chemical Behaviour of Vitamin B<sub>2</sub>.

B. C. GUHA and P. N. CHAKRAVORTY, Calcutta.

The chemical study of vitamin B<sub>2</sub> has been continued. Charcoal, fuller's earth and silica gel have been tried as adsorbents and various methods have been investigated in order to elute the vitamin from the adsorbates. Methyl alcohol with hydrochloric acid has been found to be one of the most efficient extractants. The vitamin is neither inactivated nor precipitated by bromine and is adsorbed by silver bromide. Fractionation by solvents and several precipitants has also been tried, in some cases with encouraging results.

139. Bitter Principle from *Tinospora Cordifolia*.

V. K. BHAGWAT and B. V. BHIDE, Poona.

Fluckigor (*Zeit. des Oestn. Apoth. ver.*, 1884, 312) found a trace of berberine in the bitter principle of *Tinospora Cordifolia* but did not identify the other constituents. He only found that the material when boiled with dilute sulphuric acid, gave a sugar and lost its bitterness. The hydrolytic product was not obtained in a pure crystalline condition. Three crystalline substances have now been isolated, m.p. 226–228°, m.p. 181–182°, and m.p. 81–82°. The first of these compounds is not a glucoside. When treated with acetic anhydride in the presence of pyridine, an acetyl derivative m.p. 212° is obtained but, when treated with acetic anhydride in the presence of sodium acetate, a compound m.p. 201–202°, is obtained. It absorbs bromine giving a derivative which is readily decomposed by water. Dilute nitric acid gives oxalic acid. Boiling with dilute caustic soda produces a deep blue solution which gives an orange precipitate in the presence of dilute hydrochloric acid.

140. Chemical Investigation of Indian Medicinal plants.  
Part III. The leaves of *Erythrina Indica*.S. N. CHAKRAVARTI, M. L. SITARAMAN, and A. VENKATASUBBAN,  
Chidambaram.

A complete analysis of the leaves of *Erythrina Indica* has been made. An interesting substance, m.p. 83°, has been isolated. This substance does not contain nitrogen and is a relatively inert substance. The leaves contain a mixture of alcohol-soluble alkaloids, from which a crystalline alkaloid, m.p. 117° has been isolated by extracting the alcoholic extract with acetone.

141. The Constitution of a Colouring Matter of the Leaves of *Ginkgo biloba*.

K. C. GULATI, H. S. MAHAL, and K. VENKATARAMAN, Lahore.

Comparison of the dimethyl ether (I) of a colouring matter, C<sub>16</sub>H<sub>12</sub>O<sub>5</sub>, isolated by Furukawa (1932) from the leaves of *Ginkgo biloba*, with known trimethoxyflavones derived from anisic acid and a consideration of the orientation of hydroxyl groups commonly encountered in naturally occurring flavones have led us to believe that *bilobetin* (II) is a mono-methyl ether of 3:7:4'-trihydroxyflavone (III). The Robinson reaction between  $\omega$ -methoxyresacetophenone and *p*-benzyloxybenzoic anhydride gave 3-methoxy-7-hydroxy-4'-benzyloxyflavone, treatment of which with hydrochloric and acetic acids led to the 3-methyl ether (IV) of (III). Similarly from  $\omega$ -benzyloxyresacetophenone and anisic anhydride and subsequent debenylation was obtained the 4-methyl ether (V). Neither (IV) nor (V) resembled (II) and the synthesis of the third isomer is in



progress. Starting from 2-hydroxy-4-methoxyacetophenone and *p*-benzyloxybenzaldehyde, 7-methoxy-4'-benzyloxyflavanone has been prepared and a new method for the preparation of polyhydroxychalcones and flavanones has been devised.

142. A Note on the Correlation between Chemical Structure and Pharmacological action of Embelin.

D. D. KANGA and K. S. NARGUND, Ahmedabad.

An attempt has been made to correlate the chemical structure and pharmacological action of Embelin which Paranjpe and Gokhale have found to be specific against tape-worms. Most anthelmintics hitherto reported belong to the group of phloroglucinol derivatives (Green). According to Hasan and Stedman's formula Embelin does not belong to this group. It has therefore been proposed that Green's principle correlating structure and anthelmintic properties should be extended so as to include derivatives of quinone and hydroxyquinones.

143. High boiling Phenols from Anthracene Oil.

S. K. GANGULI and P. C. GUHA, Bangalore.

The alkali extract of anthracene oil (b.p. above 350°), yielded on acidification viscous tarry acids (yield 6.67%; sp. gr. at 45°, 1.1283), which, on being distilled under highly reduced pressure, gave fractions (90°-10-200/2 mm.) the last few (150°-10-200°) being highly viscous. Isolation of individual components could not be effected by repeated fractionations, fractional precipitation from sodium hydroxide with hydrochloric acid or as derivatives of HgCl<sub>2</sub>, picric acid, etc.

Crystalline phenacyl-ethers have, however, been obtained from alcoholic solution of the sodium salts by reacting with  $\omega$ -brom-acetophenone. Phenacyl ethers from fraction 160-170° yielded, on repeated fractional crystallisation from hot alcohol, two distinct compounds m.p. 163° and 133°.

144. Chemical Investigation of the High boiling Bases from Anthracene Oil (b.p. 170-350°).

S. K. GANGULI and P. C. GUHA, Bangalore.

Of the three phenylphenacyl esters reported last year the one melting at 208° appears to be a quinoline or isoquinoline dicarboxylic ester.

The fractions b.p. 100-105°/2 mm. and 105-110°/2 mm. give a mixture of yellow crystalline picrates from which after repeated fractional crystallisation under regulated cooling within a range of 10°, it has been possible to isolate six distinct picrates, all of which have been converted into the chlorplatimates possessing sharp m.p. It is claimed that five new bases have been isolated from anthracene oil; the presence of 5:8-dimethylquinoline in it is also established.

145. Low Temperature Carbonization of Indian Coals.

S. S. GHOSH and H. K. SEN, Calcutta.

The products of low temperature carbonisation of inferior grade Indian Coals at various temperatures are discussed.



146. Extraction and Purification of Strychnine and Brucine from *Nux Vomica*.

M. S. PATEL and G. B. RAO, Bombay.

Powdered *Nux vomica* seeds have been extracted with lime and methylated spirit with 40% redistilled methylated spirit and with alcohol. Other solvents including 1 to 10% HCl have been tried. It has been found that the alkaloid content of extracts increases with the concentration. Extraction with dilute HCl gives about 10% less yield of the alkaloids than that obtained with alcohol but, as the acid extracts only the basic substances, the recovery of the alkaloids from the extracts becomes easier. Removal of fatty material and waxes from the seeds prior to extraction simplifies the acid extraction operation.

## 147. Attempted Synthesis of Cantharic Acid. Part III.

V. N. PAI and P. C. GUHA, Bangalore.

Methyl *cyclo*-hexan-3:6-dione-1:2-dicarboxylate was methylated with methyl iodide and sodamide in benzene suspension, when only the 2-methyl derivative was isolated. The copper salt of the latter did not react with methyl iodide even on heating under pressure, and the silver salt could not be prepared on account of the strong reducing action of the ketonic ester on silver nitrate. The potassium salt of the 2-methyl derivative, however, reacts to give a neutral oil, which, from its methoxyl value, appears to be a mixture of the desired C-1:2-dimethyl compound and the 2-methyl-6-o-methyl compound in equal proportions.

148. *Isoasarone*.

N. C. KELKAR and B. SANJIVA RAO, Bangalore.

The asarone isolated from *calamus* roots has been found to be a mixture of isomers of asarone. Nearly 30% of the oil has been found to be allyl-asarone (*isoasarone*), which is a liquid. Only solid potash above 200° converts the liquid asarone into the solid asarone (m.p. 61-62°). On treatment of the asarone mixture with mercuric acetate a mixture of glycols was obtained. Allyl-asarone has not till now been known to occur in nature. The properties of the product have been compared with the synthetic *isoasarone*.

149. *Ventha-velichchenna*, the oil from coconut milk.

B. H. IYER, Bangalore.

The milky juice obtained from the kernal of ripe but undried coconut, yields, on heating over a free flame, a colourless or light yellow oil possessing a very agreeable and appetizing odour. Four coconuts yield 135 g. of the oil which is a medicine indigenous to Malabar and is a household remedy for many ailments.

The saponification value of the oil is 232 while that of the mixed acids is 277. On separating the unsaponifiable part of the oil by soxhleting the dried soap with petrol (b.p. 50-60°) a liquid (b.p. 120-140°) with an odour resembling that of a hydrocarbon has been obtained.

150. *Cashew-nut* shell oil and its Condensation products.

L. GOPALA RAO, Bangalore.

Various known methods of extracting the oil from the shells without injury to the kernels were examined, and it was found that by treatment of the nuts at 200°, or at 160° after abrading the shells, a large percentage (70-80 per cent.) of the oil can be recovered in a satisfactory condition.



The methods at present adopted in commercial practice are deemed unsatisfactory, if only in point of yield.

The oil (cold-pressed) as also the constituents, viz. anacardic acid and cardol, were examined with a view to ascertain the extent to which prolonged treatment at 200–250° affects the chemical properties and varies the nature of the condensation products.

Anacardic acid condenses with hexamethylene-tetramine very slowly and the resulting resin sets at a temperature above 150°, or at 200° in case of the heated acid. Cardol condenses readily yielding a dark resin which brightens to purple on curing. The cold-pressed oil as also commercial specimens yield satisfactory oil-soluble resins which can be rendered infusible and resistant to drastic chemical action. The main difference between the resins from cold-pressed, as against commercial oils lies in the critical hardening temperatures, 120° in case of the pure oil and 200° with commercial oils.

### 151. Extraction of Saponins from Soap-Nuts, *Sapindus Trifolius* and Soap-Pods *Acacia Concina*.

M. S. PATEL and M. C. LAIWALA, Bombay.

Soap-nuts have been found to consist on the average of about 58% pericarp and 42% stone. The saponin content of the pericarp is about 6.8%. Various methods are being tried to find out a simple and economic process of extraction. Water, alcohol, and methylated spirit have been tried as solvents. Attempts are being made to separate tannins and saponins by fractional precipitation. Preliminary removal of fats and waxes from the pericarp facilitates the extraction of saponins.

### 152. Isopsoralen from the Seeds of *Psoralea Corylifolia*.

H. S. JOIS and B. L. MANJUNATH, Bangalore.

With *Psoralen* (*Jour. Indian Chem. Soc.*, 1933, 10, 45) a small amount of an isomeric compound (*Isopsoralen*,  $C_{11}H_8O_3$ ) occurs in the solid material which separates from the oil obtained by the extraction of the seeds of *Psoralea Corylifolia* with petroleum. The separation of the two is effected by repeated fractional crystallisations from alcohol and chloroform. *Isopsoralen*, m.p. 141–142° is also lactonic and like *Psoralen* can be crystallised from boiling water. Methyl sulphate gives the methyl ester of *methoxy-isopsoralic acid*, from which the free acid was obtained by saponification.

### 153. The Chemical Examination of the Roots of *Aristolochia indica*. Part III.

S. KRISHNASWAMI, B. L. MANJUNATH, and H. Y. SARANABASAPPA, Bangalore.

The yellow compound isolated from the roots of *Aristolochia indica* was found to have the formula  $C_{15}H_{10}O_7$  (m.p. 276°). It is intensely bitter and is sparingly soluble in most of the usual solvents but can be crystallised from a large quantity of alcohol or glacial acetic acid.

It is readily decomposed by cold concentrated sulphuric acid and methoxy groups are absent. Carbon dioxide precipitates it from dilute alkaline solution but it is not a phenol and cannot be acetylated, benzoylated or methylated.

The alkaloidal constituent of the roots,  $C_{24}H_{25}O_4N$  has been subjected to detailed chemical examination.



154. Active Principles from the Fruits of *Solanum xanthocarpum*.  
(Bhuringini.)

I. Z. SAIYED and D. D. KANGA, Ahmedabad.

The powdered dried fruits were successively extracted with petrol and alcohol.

From the petrol extract a gluco-alkaloid (A) (m.p.  $245^{\circ}$ ) has been isolated. This on hydrolysis gave a sugar which has not been identified and a solid m.p.  $165-167^{\circ}$ .

The alcohol extract on concentration gave a solid (B) (m.p.  $238-239^{\circ}$ ). The residue after removing (B) was separated into basic and non-basic portions. The non-basic portion after purification gave a crystalline compound (C) (m.p.  $217-220^{\circ}$ ). The basic portion gave two crystalline compound (D) m.p.  $265^{\circ}$  and (E) m.p.  $196^{\circ}$ . The substance (E) was one of the products of incomplete hydrolysis of the alcoholic extract, the other product being a sugar. This substance on further hydrolysis gave a sugar and a crystalline compound (m.p.  $215-17^{\circ}$ ).

155. The Drying of Mango Pulp.

M. S. PATEL and S. D. AGNIHOTRI, Bombay.

Mango pulp has been dried under various conditions of temperature and pressure. It has been found that only the pulp dried at temperatures lower than  $55^{\circ}$  gives good product. Drying under ordinary atmospheric pressure even at lower temperature discolours the product. Drying under lower pressures at temperatures higher than  $55^{\circ}$  also gives a darker product. Drying at  $50^{\circ}$  and under 10 mm. pressure yields a product which is friable and has the natural colour of the pulp as found in the fresh, ripe mango. The rate of moisture absorption by the dried pulp has been studied.

Results show that there is a great possibility for developing the mango pulp drying industry in the Bombay Presidency.

156. Cellulose from Rice Straw by Pomilio Process.

M. S. PATEL and W. V. KOTASTHANE, Bombay.

Study of the literature on the production of cellulose by chlorine process has been made. Cellulose content of samples of rice straw available in Bombay has been determined. Straw is being treated with chlorine under various conditions to find the optimum conditions. Further work on those factors that would enable the working out of economics for a semi-commercial plant that could be run by the process will be undertaken.

157. Cashew-nut shell Oil and its Industrial Utilisation.

M. S. PATEL and N. M. PATEL, Bombay.

The oil as obtained from the cashew-nut roasters is a black viscous liquid having a peculiar smell. About 60% of the oil is soluble in petroleum ether and alcohol. The residue when extracted with acetone yields resinous material, about 7 to 8% of the oil, melting at  $183-185^{\circ}$ . The oil also contains iron salts. The iron content of the oil is about 3%. Shell oil from raw nuts has been extracted. Analyses of the shell oil from roasted nuts and raw nuts are given.

158. Preparation of Camphor from Pinene.

B. G. S. ACHARYA and T. S. WHEELER, Bombay.

Continuing previous work the yield of pinene hydrochloride from pinene has been increased from 76% to a maximum of 85%. The



numerous patents on the production of camphene from pinene hydrochloride have been examined but the maximum yield of 83% of the theory obtained by the use of sodium phenoxide, sodium cresyloxide, and sodium  $\beta$ -naphthoxide has not been improved upon. The conversion to borneol of camphene through bornyl acetate does not give yields better than 64%. However, it seems possible that the conversion of bornyl acetate to borneol may be increased by the use of solid sodium hydroxide.

Quantitative yields of camphor from borneol can be obtained by the use of 50% nitric acid. The overall yield of camphor from pinene is 27%.

Contrary to statements in patent literature, it has not been found possible to convert directly pinene to camphene, or pinene hydrochloride to camphor, but the direct oxidation of camphene to camphor is promising.

Conversion of pinene direct to bornyl acetate is unsatisfactory but conversion *via* bornyl salicylate gives better results, particularly if solid sodium hydroxide is used for the preparation of borneol from the ester. (yield 18.5%.) Attempts to replace salicylic by other acids like tetrachlorophthalic and oxalic acids have been unsuccessful.

#### 159. Studies on the Fumigation of Shellac Films.

M. VENUGOPALAN, Namkum.

An investigation on the effect of certain industrial gases and chemical fumes on shellac varnish films has been made with a view to improving their properties with respect to water resistance, gloss, adhesion, etc. Hydrochloric acid and sulphur compounds like sulphur chloride, carbon disulphide and sulphur dioxide resulted in improved properties, in that the films were resistant to water and alcohol and possessed a fair degree of gloss and adhesion.

Formaldehyde, ammonia, carbon dioxide, etc. induced definite deterioration in the property of water resistance even though they improve the gloss and adhesion of the dry film.

Films exposed to nitric oxide, chlorine, etc. are considerably affected both in the dry as well as in wet condition after exposure to water.

It is suggested that this method of fumigating the articles coated with varnish, particularly by exposure to the fumes of sulphur chloride and carbon disulphide might find a useful application for making them durable and weather proof.

#### 160. Methods of preventing the Formation of Mosses on Polastered Wall Surfaces.

S. K. GHOSE, Arrah.

Exposed wall surfaces of buildings become covered with *funaria*. Methods of preventing their occurrence initially, as well as removing them when once they have appeared are discussed giving results of experiments in that direction. The use of a 4% solution of copper sulphate in the mixing water is advocated.

#### 161. Prechlorination for Algal Trouble in drinking water.

P. D. DALVI, Jaipur.

During the hot days of summer, uncovered coagulation tanks developed algae profusely and imparted smell to the water. This involved the frequent cleaning of the tanks and incurred great waste of water. Addition of bleaching powder to the water in suitable doses stopped the growth almost entirely. A 30-gallon wooden barrel with necessary fittings to mix the bleaching powder and deliver the dose, served the



purpose. The treatment, besides stopping algal growth, reduced the load on the filters to a minimum and consequently produced a higher quality of water. The dose of bleaching powder containing 25–30% of available chlorine, was between 1 and 2 parts per million. The cost of treatment was comparatively small.

#### 162. Detection of Imperfect Circulation of Water in Pipes.

P. D. DALVI.

The relation between the iron content, turbidity and total count in piped waters led to the use of these measurements to detect improper circulation of water in service pipes.

A water of imperfect circulation had always a relatively larger iron content and other impurities. A measurement of one of these, especially turbidity (this is done in less than 5 minutes) served to locate such troubles readily.

#### 163. A Note on the Separation of Shellac Constituents.

M. VENUGOPALAN, Namkum.

The work of Harries and Nagel on the preparation of several modifications of shellac has been reviewed. During the course of preparing one of their modifications by exposing shellac to the fumes of hydrochloric acid, it has been found that a small portion of shellac was unaltered so far as its fusibility and solubility in alcohol are concerned. This soluble portion could, however, be separated by extracting the HCl-exposed shellac three or four times with alcohol. On examining the alcohol-soluble portion in detail it is found to be identical in composition and properties with the normal ether-soluble resin present in shellac. The residue left after extraction with alcohol was practically colourless and possessed the same properties as pure resin.

The possibility of using this method for preparing pure or ether-soluble resin in commercial quantities without the use of a costly volatile solvent like ether and complicated apparatus has been discussed.

#### 164. Physiological Products of the Lac Insect. Part III. A Study of 'Phunky' lac wash liquor.

N. K. RANGA RAO, Bangalore.

Most wash liquors from Northern India employing 'Ari' are rich in nitrogen and 'fats'. In South India and in some North Indian factories not having a surplus brood lac, the raw material is 'Phunky'. A comparative study has been made of the wash liquors. The amounts of water and butyl alcohol-soluble nitrogenous substances have been found to be equal in 'Ari' and 'Phunky' lacs but free tyrosine, which occurs to the extent of 2.5% in 'Ari' lac, is absent from the 'Phunky' lac wash.

The nitrogenous bodies are simple polypeptides as indicated by the low ratio of 'total' to 'amino' nitrogen.

Laccaic acid in the mixture can be isolated as the barium salt.

Feeding experiments indicate that nitrogenous bodies are not suitable for the nutrition of albino rats, and that laccaic acid is excreted unchanged.

#### 165. A Note on the Use of Shellac Solutions as a Vehicle for Pigments.

N. NARASIMHA MURTY, Ranchi.

Shellac solutions are used as vehicles for making quick drying paints. The pigments used and found suitable for incorporation are lithophone,



blanc-fixe, chrome yellow, Chinese blue, lamp-black, etc. Copper carbonate was found unsuitable. Though the pigment in shellac paints settled down on storing they could be worked up again. High boiling solvents while improving the paint from the point of view of levelling, have the disadvantage of making the film slow-drying. Shellac paints are best suited for decorative work on wood and paper surfaces. Baked shellac paints on metal surfaces have improved adhesion and water resistance, but are very brittle. A shellac paint on a metal surface serves as a good under-coat for pyroxaline or dammar lacquer.

166. Dilatometric Studies in Enzyme Action. Part VIII.  
Hydrolysis of Alanine anhydride.

M. SRINIVASAN and M. SREENIVASAYA, Bangalore.

The alkali hydrolysis of the 2:5-diketopiperazines dilatometrically studied in the first instance with glycine-anhydride (*Proc. Indian Sci. Congress, Patna, 1933*), has been extended to alanine anhydride. This diketopiperazine, obtained in the racemic form by heating *D*-alanine with glycerol (Balbiano and Trasciati) has been treated with varying strengths of alkali in the dilatometer and the increase in volume accompanying the reaction measured at known intervals. The kinetics of the reaction have also been followed independently by an estimation (Van Slyke) of amino groups. A linear relationship between the release of amino groups and volume change has been obtained except in the initial stages where some abnormalities are observed. This initial abnormal change appears to be dependent upon the strength of the alkali used. The final volume change, as was observed in the case of glycine anhydride, is of the order of 7.5 c.c. per amino group released.

167. A Dilatometric Study of the Papain Digestion of  
Proteins.

M. SREENIVASAYA, B. N. SASTRI and H. B. SREERANGACHAR,  
Bangalore.

Enzymic digestion of proteins can be followed in the dilatometer. It is accompanied by a progressive depression in volume. The kinetics of gelatin hydrolysis by papain and also by papain activated by hydrocyanic acid have been investigated in the dilatometer. The depression obtained by the gelatin-papain-hydrocyanic system is about five times that obtained by a system in which the activator is not employed. The kinetics have been followed simultaneously by a determination of the amino nitrogen at definite time intervals.

168. A new Thermophilic Bacterium for Dissolving Sugars and  
Hemicelluloses.

G. C. DAS GUPTA, R. N. CHATTERJEE and H. K. SEN,  
Calcutta.

A thermophilic bacterium has been isolated from horse dung at 55° which appears to be distinct from those of Viljoen and Langwell. Recent culture shows the following characteristics:—

It is short, rod-shaped, non-motile and spore-forming. It measures about 4.5  $\mu$  in length, and 0.75–0.8  $\mu$  in breadth, the oval spore being fixed to one end of the rod. The spores are generally found to be about 2  $\mu$  in length and 1  $\mu$  in breadth. At 55° it ferments both hexoses and pentoses, and has the power of decomposing cellulose, especially in a modified condition. So far as the rate of fermentation is concerned, its action on hemicelluloses is similar to that on the sugars. At lower temperatures, however, the bacterium has no fermentative reaction.



The products of fermentation are alcohol, butyric acid, formic acid, acetic acid and carbon dioxide. Of the total acid, 30% is butyric, 25% formic, and 45% acetic acid. The yield of alcohol varies from 3.0% in the case of arabinose to about 12.0% in the case of water hyacinth. The technical possibilities of the bacterium have been discussed.

#### 169. Dilatometric Studies in the Enzymic Degradation of Proteins.

H. B. SREERANGACHAR, B. N. SASTRI and M. SREENIVASAYA, Bangalore.

In a recent communication (unpublished) a study of the kinetics of tryptic digestion of casein and gelatin as followed by the dilatometer and the gasometric method of determination of amino nitrogen has been given and the relation between the dilatometric depression and the amino nitrogen increase has been obtained. In continuation of this work, the carboxyl groups released at different stages of the reaction have been estimated by the alcohol titration method of Willstätter and Waldschmidt-Leitz. The ratio between the carboxyl release and the amino nitrogen is strictly unity only in the case of gelatin. The relation between the dilatometric depression and the carboxyl groups released has been established.

In the case of casein the undigested protein has been estimated at different stages by precipitation with tri-chloroacetic acid. The quantity of protein hydrolyzed bears an interesting relationship to the dilatometric depression.

#### 170. The Amylase of Banana.

B. N. SASTRI and G. R. Row, Bangalore.

The ripening of the banana is accompanied by progressive disappearance of starch and accumulation of sugars. The mechanism of this process has been a matter of controversy. Tellaries and Bailey claim to have shown the presence of a diastase while Falk and McGuire, and Ranganathan have not been able to demonstrate the presence of the enzyme. A critical examination of the question has revealed that the pulp does not appear to contain any amylase which is confined to the skin. Acetone-treated skin, on extraction with a one per cent. solution of peptone, yields an active preparation of amylase which has been found to hydrolyse banana starch.

#### 171. Urease Activity of Leguminous Seeds on Germination.

B. N. SASTRI and B. A. SUNDARA IYENGAR, Bangalore.

It is generally recognised that, on germination, the urease activity of leguminous seeds is enhanced. Viswanath has shown that the urease activity of *Cajanus indicus* increases on germination. The increased activity may be due to (1) an increase in the concentration of the enzyme, (2) the formation of activators, or (3) an increase in the case of extraction. These possibilities have now been critically examined. It has been shown that the increased urease activity is not due to an absolute increase in the concentration of urease or to the formation of activators but due to the enhanced facility with which the enzyme can be extracted after germination. This conclusion has been confirmed in the case of a number of legumes.



## 172. Role of Cyanogenetic Glucosides in Plant Metabolism.

M. SREENIVASAYA, Bangalore.

When activated by hydrocyanic acid papain brings about a further degradation of proteins. This activator is possibly provided by the emulsin hydrolysis of cyanogenetic glucosides occurring in plants and it was of interest, therefore, to obtain experimental evidence in support of this theory. A mixture of papain and emulsin was allowed to act on gelatin to which a small proportion of amygdalin was added. A control experiment in which amygdalin was absent was also conducted. Results show that gelatin digestion is definitely activated in presence hydrocyanic acid developed by the simultaneous hydrolysis of amygdalin.

## 173. Amylase from sweet Potato.

K. VENKATA GIRI, Bangalore.

A very highly active diastatic enzyme which hydrolyses starch into sugars is present in the sweet potato. Attempts have been made to isolate the enzyme in a concentrated form.

A very active preparation can be obtained from the water extract of the meal obtained from the sun dried material by precipitation with alcohol. The activity of this preparation compares very favourably with that of the diastase preparation obtained from barley malt prepared similarly.

The enzyme acts best in the region of  $P_H$  4.8–6.0 (optimum temperature 50–55°). The temperature coefficients of the reaction of the sweet potato amylase on starch have been investigated between 20–70°. Other properties of the enzyme, including the activation by salts have been investigated.

The inner portion of the tuber has greater amylolytic activity than the surface layers. On dialysing the expressed juice in collodion bags, the activity per unit weight of the dry residue is increased nearly five times.

The change in the amylase content of the tuber on storage and its bearing on the physiological changes taking place in the tuber have been discussed.

174. Digestibility of Proteins *in vitro*.

H. B. SREERANGACHAR, B. N. SASTRI and M. SREENIVASAYA, Bangalore.

The proteins from three pulses, *Phaseolus mungo*, *Phaseolus radiatus* and *Dolichos lablab* have been subjected to tryptic hydrolysis under standard conditions and their relative digestibility has been followed both by the dilatometer and the amino nitrogen determination method of Van Slyke.

175. Studies in the Proteins of Indian Foodstuffs. The Proteins of *Lathyrus sativus*.

Y. V. SREENIVASA RAO, Bangalore.

The chief proteins of *Lathyrus sativus*, popularly known as Khesari, are an albumin and a globulin. The former contains 17.2% of nitrogen and 0.88% of sulphur. The latter contains traces of phosphorus, 16.8% of nitrogen and 0.39% of sulphur. A study of the distribution of nitrogen in the globulin yielded the following results: humin, 0.5; amide, 9.6; basic, 35.7; and non-basic, 54.2% respectively. Cystine was present to the extent of 0.56% and tyrosine, 2.84%. Tryptophane was present in traces.



### 176. The Precipitation of Anti-bodies from Anti-rinderpest Serum.

J. R. HADDOW and K. C. SEN, Muktesar.

In a recent paper (*Ind. J. Vet. Sci. and Anim. Husbandry*, 1933, 3, 149) a number of methods for fractionating the anti-bodies of anti-rinderpest serum were studied. Since then we have carried out a large amount of work with various serum fractions prepared according to different methods and have tested them on animals susceptible to rinderpest virus. It has been found that alcohol gives a good separation of the anti-bodies at 0°C., and that this fraction can be dissolved in normal saline and used in inoculation work on animals without any appreciable loss of potency. It is also possible to concentrate the anti-serum in this way to about 5 times the original strength. Under certain conditions, a low potency serum can also be concentrated sufficiently to be useful for preventive inoculations.

### 177. The Analysis of Ghee.

C. B. ALMOULA, Karachi.

It is suggested that for genuine cow ghee or cow and buffalo ghee the following limits should be fixed for the constants named:—

Reichert Meissl value—not less than 24.0.

Polenske—not less than 1.0 and not more than 4.0.

Saponification value—not less than 224 and not more than 230.

Butyro-Refractrometer reading—not less than 41.0 and not more than 44 at 40°C.

The influence of admixture of (a) vegetable product, (b) coconut oil, and (c) mineral oil on these constants has been determined. The author suggests that vegetable product should be coloured by dye by which it could be identified.

### 178. Estimation of Carbonates in the Soil.

T. R. SESHADRI, Waltair.

A simple and rapid gravimetric method is described. The conditions for the complete decomposition of the carbonates without introducing errors due to the presence of soil organic matter or sulphides have been studied using different kinds of soils.

### 179. The Colour of Cotton-flowers.

T. R. SESHADRI, Waltair.

A remarkable difference in the pigmentation of the flowers of Cambodia (*G. Hirsutum*), Uppam (*G. Herbaceum*), and Karunganni (*G. Indicum*) has been noticed. The first is very pale (ivory coloured) whereas the other two are golden yellow. It is found that this difference cannot be explained as due to the quality or quantity of the pigments present in the different flowers. Perkin's suggestion that the yellow of flowers is due to the existence of the flavonols in the form of potassium salts is not found to be tenable in the present case. From an examination of different reactions of the aqueous extracts of the flowers, it is shown that the differences could be attributed to co-pigmentation which affects particularly the hydroxyl group in the 3 position.

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## ABSTRACTS OF PAPERS.

### Section of Zoology.

*President :—Prof. P. R. Awati, B.A. (Cantab.),  
D.I.C., I.E.S.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Zoology.

### Abstracts.

1. Studies on the ciliate, *Conchophthirus lamellidens* Ghosh, from the gills of a fresh-water mussel.

H. N. RAY and M. CHAKRAVARTY, Calcutta.

The morphology of this ciliate is described in detail. Presence of morphonemes have been demonstrated by various methods of staining. Structure comparable to neuromotor apparatus of *C. mytili* DeMorgan, described by Kidder, is not found to occur in this ciliate. Its method of feeding on gill-cells and sperms of the host has also been described in detail. Nuclear organization prior to binary fission and conjugation has been studied. The method of conjugation is different from what has been described in the case of *C. mytili* by Kidder in 1932. The chromatin contents of the nucleus, as shown by Feulgens reaction at various stages of its life-history, have also been studied in some detail.

2. A new Species of the genus *Helicometra* from the intestine of *Trigla gurnardus*.

G. S. THAPAR and J. DAYAL, Lucknow.

The material for the present paper was collected by one of us from the intestine of *Trigla gurnardus* that died in the aquarium of the Zoological Society of London.

Various species of the genus *Helicometra* had been described, but Nicoll (1915) after careful consideration came to the conclusion that there is but one species of the genus—*H. pulchella*, all others being synonymous with it. The writers fully agree with this view.

The present species is interesting as it presents many differences from the type species, particularly in the shape and position of the cirrus and cirrus sac; the relative length of the pharynx and the œsophagus; the position of the testes and the genital pore; and the distribution of the yolk glands. All these differences, along with a few other minor points dealt with in the paper indicate that the species is new to science.

The name *Helicometra gurnardus* n.sp. is proposed for this new form.

3. On a new Trematode parasitic in the intestine of *Hardella thurgi*.

B. B. SINHA, Lucknow.

(Communicated by Dr. G. S. Thapar.)

A large number of worms were obtained from the small intestine of *Hardella thurgi* at Lucknow. These worms, on examination, appear to belong to the family Pronocephalidæ, and are interesting because they exhibit characters that connect the two subfamilies, Pronocephalinæ and Caraxicephalinæ, and justify their fusion under one name. A good deal of work has been done on this family, the earliest being that of Looss (1899). Since then much valuable work has been done, particularly by Price (1930).

The present new form is characterized by having boat-shaped body, concave ventrally; a simple collar; two posterior conical projections;



glandular papillæ covering the ventral surface in longitudinal rows; and two longitudinal rows of testes, preovarial and postovarial in position. A detailed account of the anatomy of the genus is given and is followed by a discussion on the position of the new form.

4. On a new Trematode genus of the family Spirorchidæ from the vascular system of *Hardella thurgi*.

B. B. SINHA, Lucknow.

(Communicated by Dr. G. S. Thapar.)

The worms were collected from the larger blood vessels of the tortoise, *Hardella thurgi*, at Lucknow, and belong to the family Spirorchidæ. They resemble in general features the genus *Spirorchis*, from which they can be readily distinguished by the presence of a ventral sucker and the intestinal loop at its origin at the anterior end. In the presence of the ventral sucker, they resemble the genus *Vasotrema*, but differ from it in the presence of the intestinal loop, preovarial position of the testes and the postovarial position of the genital pore. The only other known genus of the subfamily Spirorchinæ is *Unicæcum*, from which it can be separated by the presence of both cæca, the presence of the ventral sucker, postovarial genital pore and the anterior intestinal loop. The present genus, therefore, appears to connect the already known genera of the subfamily Spirorchinæ, and can be readily distinguished from them in the characters enumerated above.

A detailed account of the anatomy of the worm is also given.

5. The bladderworm parasites of cattle in Lahore.

D. A. KUMAR and SUKH DYAL, Lahore.

During the course of collection the authors have noted five types of bladderworms, of which *Echinococcus* is the most common. It has been found in the liver, spleen, kidney, lungs and mesentery, liver being attacked most commonly. One bladder had attained the size of a football. Another type of bladderworm is solid and hard, and is a conglomeration of small bladders. It is, however, rare and was discovered from the liver. Another common type is the *Polycercus*, bladders being found floating freely in the thoracic and abdominal cavities. A subtype of this is found lodged in the mesenteries. The last is the *Cænurus* type which has so far been described from the brain and subcutaneous tissue of sheep, goat, and rabbit. The authors have found it in the mesenteries of a cow. Seasonal variations and the effect of parasites on the hosts have also been observed.

6. Observations on the tapeworms *Avitellina lahorea* and *Helictometra* from Lahore.

D. A. KUMAR and SUKH DYAL, Lahore.

*Avitellina lahorea* was described from Lahore by Woodland who gives sheep or goat as its probable host. The authors have found it as a common parasite in cows. The largest specimen in the collection is 18 feet in length. In addition to the description of the head and other systems of the parasite the eggs of this species have been figured and described.

Genus *Helictometra* has so far been described from the cattle of Europe, Africa, and America. The authors found two specimens of this genus in the intestines of cows. *Helictometra giardi* is the nearest species to the present form. In *H. giardi* (Moniez) the uterus is undulating. In the Lahore form the uterus is straight, but develops pouches on each side at maturity. A detailed account of the worm has been given.



7. On the nematode causing stomach tumours of the Indian crocodile, *Crocodilus palustris*.

G. D. BHALERAO, Muktesar-Kumaun.

The worms causing tumours of the stomach wall of a crocodile shot at Jullundur have been identified as *Multicæcum agile* Wedl. This is the first record of these worms from a locality outside Egypt.

The worms present many interesting morphological features particularly in respect of the alimentary canal: the intestine having an anteriorly directed cæcum and the œsophagus possessing a small ventriculus from which arise two anterior and three posterior appendices.

The description of the species, which was incomplete in some respects, has been thoroughly revised.

8. Some observations on the common earthworm of Poona.

T. G. YEOLEKAR and H. S. RAI, Poona.

*Pheretima posthuma* has not so far been found and recorded from Poona. The earthworm which is commonly found is *Pheretima elongata*. The authors have noted variations in the number of spermathecae and in the accessory glands of this worm.

It is interesting to note that the earthworm found on the north-east bank of the Mulla river and Deccan College side belongs to the Genus *Eudichogaster*.

9. A note on the polypoid (Cephalonion) galls of *Pongamia glabra* Vent.

M. S. MANI, Calcutta.

The polypoid (cephalonion) galls on the leaflets of *Pongamia glabra* Vent. have been wrongly described by previous workers to be formed by the mite, *Eriophyes cheriani* Mass. In this note the author has adduced experimental evidence to show that though found in the gall, the mite is not primarily responsible for its formation. The gall is originally formed by a minute undescribed Itonidid (Cecidomyid) fly and only certain minor changes in the gall are produced by the mite.

10. An annotated list of the Ichneumon wasps noted from South India.

T. V. RAMAKRISHNA AYYAR and K. BRAHMACHARI, Coimbatore.

Considerable amount of interest is now being evinced by economic zoologists in what is called the Biological method of pest control which consists in utilizing a parasite or a predator to control the pest. Among friendly animals which help man in this control work parasitic wasps play a very prominent rôle. And in order to enable workers to properly utilize these creatures a good deal of preliminary work in the way of systematic and ecological studies have to be carried out. This paper is intended to be a continuation of the work of the senior author on the bionomics and systematics on Indian parasites; papers have been published by him before on the Braconidæ, Chalcidæ and on the known economic parasites. In this paper an attempt is made at making an up-to-date reference list of the Ichneumon wasps known from S. India with whatever the writers have been able to add in the shape of observations during their recent studies of this interesting group. This is the first list of the kind on this group for S. India and it is hoped it may help to some extent those embarking on the study of these insects. It may be added that apart from the economic importance of the group,



there is the purely biological and scientific interest of such a faunistic and ecological study on one of the most highly organized group of insects—the Ichneumon wasps.

11. On the bionomics of a bag-worm on banana (*Acanthopsyche* sp.).

K. BRAHMACHARI, Coimbatore.

The name bag-worm is generally applied to the caterpillars of the family Psychidæ, because of the characteristic habit of these caterpillars carrying bags with them. There is pronounced sexual dimorphism among them in that the males are normal while the females are degenerate vermiform creatures. The group has not attracted the attention of the Entomologists in India since it rarely occurs as a regular pest of cultivated crops. Though there are references to Psychids causing damage to tea plants, no detailed life-history of any species has been recorded so far. This paper deals with one of these which was found causing appreciable damage to banana in Madras.

12. First record of the Chalcid genus *Comperiella* H. from India (*C. indica*, sp. n.).

T. V. RAMAKRISHNA AYYAR, Coimbatore.

In 1906 the genus *Comperiella* was erected by L. O. Howard to include an extremely interesting Chalcid wasp collected by the famous parasite hunter George Compere from China and the type was named *C. bifasciata*. Since then three more species of this genus have been described, one from Australia *C. pia* by Girault in 1915, the second *C. ceraptocera* by Mercet from Spain in 1921 and the third *C. unifasciata* by Ishi from Japan in 1925. The genus has not been recorded from India till now. A couple of years ago, while the author was engaged in the bionomic and systematic studies on South Indian scale insects and their parasites, one of the many novelties he came across was a wasp bred from a diaspine scale insect which on examination was provisionally regarded as a *Comperiella*. Due to want of time and sufficient material further examination of the insect was left in abeyance though a record of it was made in the author's bulletin on Coccidæ in 1930. Recently the study was taken up on further material becoming available and on comparison with the description of the three previously recorded forms it was found to be a distinctly new species. Being new to India and belonging to a beneficial group of insects the writer has described the insect in this paper under the name *Comperiella indica*, sp. n.

13. On the development of the peritrophic membrane in *Aedes* (*Stegomyia*) *albopictus* Skuse (Diptera).

P. SEN, Calcutta.

Divergent views are held as to the origin of the peritrophic membrane in insects. The author has previously shown in another group of dipterous insects, the Cecidomyiidae, that this membrane is formed by the secretion of the mesenteric epithelial cells. Its formation in the *Aedes* mosquitoes has now been worked out and it has been noted that in origin the membrane differs very little from that of the Cecidomyiid, *Simulium*, *Psychoda*, and *Drosophila* as recorded by some previous workers.



#### 14. The development of the female efferent ducts in *Apis* and *Melipona*.

C. J. GEORGE, Bombay.

During the larval stages the ovaries are situated on the 6th segment and the oviducts extend as thin strandular chords till they reach the 7th segment where they terminate in enlarged knobs and rest on the hypodermis.

During the early pre-pupal stage two median invaginations arise on the ventral side, one behind the 7th abdominal segment and the other behind the 9th. The anterior one extends forward, and, as it approaches the oviducts, bifurcates into two. The two resulting ducts meet the oviducts of their respective sides and ultimately fuse with them, thus establishing an opening to the outside. The vaginal opening at this stage lies behind the abdominal segment VII. The invagination behind the 9th abdominal segment develops into the acid and alkaline glands of the sting.

The vaginal opening which in the prepupa opens on the 7th gets later on shifted to the 8th. This takes place either by a definite invagination from the 8th segment (the spermatheca) which meets the vagina anteriorly or by the development of a groove extending from the vagina backwards and the gradual closing of this groove to form a tube or by the combination of these two processes. The vagina as a result of these changes comes to lie behind segment VIII. This process consists of (1) the development of an extension tube from the 7th to the 8th, (2) the development of a spermatheca.

This study further supports the author's findings given elsewhere that the primitive median vaginal opening was situated on the 7th segment.

Nel places the primitive spermatheca on segment VIII and criticizes Singh-Pruthi for locating it on segment IX. From the author's observations he postulates that primitive insects had spermathecae on segments VIII and IX and possibly on VII also. In some that on the 8th was retained, the 9th one having lost its spermathecal function and retained only the glandular function. In other more evolved insects the 8th one was absorbed into the development of the vagina posteriorly and that on the 9th was retained. *Blatella* is an example where spermatheca is present on the 7th segment (Nel).

#### 15. The metamorphosis of the ventral nerve chord in *Apis* and *Melipona*.

C. J. GEORGE, Bombay.

On the ventral nerve chord of the larva there are 3 thoracic and 8 abdominal ganglia. According to Nelson there are 3 thoracic and 11 abdominal ganglia in the embryo. He states that the abdominal ganglia numbers 8, 9, 10, and 11 fuse into a composite one later. Thus, excepting the last, all the ganglia are single ones.

During the pupal stage soon after defæcation the 1st abdominal ganglion moves forward and fuses with the metathoracic one. During a later stage when the legs and mouth-parts are about to unfold themselves, the 2nd abdominal ganglion moves forward and fuses with the preceding one. At this stage the penultimate ganglion, i.e. ganglion 7 moves forward and fuses with the 6th and comes to lie in the 6th segment. During the pupal stage, the compound ganglion of the meta-thorax fuses with the ganglion of the mesothorax and the composite ganglion comes to lie in that segment. Thus the adult ventral nerve chord is derived. The process described as 'moving forward' takes place by the shortening of the double nerve chord.



Snodgrass' account given on page 293 of his book 'Anatomy and Physiology of the Honey Bee' agrees with the foregoing. But he fails to reconcile the adult anatomy with the changes taking place during metamorphosis. According to him the penultimate ganglion of the adult bee lies in the 6th segment of the abdomen and innervates that segment. Specimens of *Apis dorsata* were dissected to see if the above statement was correct. It was found that the 6th abdominal ganglion gave rise to two pairs of nerves, as might be expected from its composite nature, of which the anterior pair innervated the 6th segment and the posterior pair the 7th segment. Snodgrass' description on page 237 is therefore obviously incorrect.

#### 16. On the reproductive system of Bruchid beetles.

D. D. MUKERJI and M. A. HAKIM BHUYA, Calcutta.

In continuation of the work on the Bruchid beetles read before the Agricultural Section, Twentieth Science Congress, the authors have investigated in detail the anatomy and the histology of the reproductive systems of the two species common in the locality, viz. *Bruchus (Pachymerus) chinensis* and *B. quadrimaculatus*. While there are not many differences in the number and disposition of testes in the above two species, the shape and armature of the ejaculatory duct in each species are distinct. In the female reproductive system the number of ovarioles and the shape of the bursa copulatrix are different in the two species. The bursa copulatrix is large in these beetles and is provided with a pair of inside valves which prevent the passage of the penis within the upper lumen of bursa copulatrix. The spermatheca opens into the vagina anterior to the opening of the oviduct and receives the duct of the accessory gland which is long and slender. Attempt has also been made to study the function of the bursa copulatrix, by killing and taking serial section of the reproductive organ while the insects were engaged in copulation, as well as before and after egg-laying.

#### 17. Preventing damage by termites in buildings in India.

S. K. GHOSE, Arrah.

In this paper the author reviews the behaviour and systematy of termites in India in general, with special reference to the species met with in Bihar and Orissa, and suggests measures found successful in minimizing risks of attack and also specific methods for making termite-proof buildings in which cement, non-corroding metal barriers, paradichlorobenzene and other chemicals are effectively used.

Specimens of 'white ants', their queens and nests, as also specimens of attacked timbers will be exhibited in the meeting.

#### 18. Diapause in the Mealy-bug *Monophlebus*.

MOHAN SINGH.

The phenomenon of diapause in insects has not hitherto been investigated in India. Mealy-bugs (*Monophlebus*) offer suitable material for this study.

The paper contains results of experiments for determining the effects of temperature, moisture, evaporation, and light on diapause.

#### 19. Probable functions of the various parts of the nervous system of the Ak grasshopper (*Pæcilocerus pictus*).

SHAM SINGH.

This study was made by damaging different parts of the nervous system with an aseptic needle, and observing the effects of the operation on the general behaviour and activity of the insect.



The supracæsophageal ganglion seems to be the central organ of sensation. The subcæsophageal ganglion has no co-ordinating function but is chiefly concerned with the control of the movements of the mouthparts. Each ganglion of the ventral nerve-chord is an independent reflex centre, and controls respiratory movements in its own segment.

20. Preliminary observations on the ecology of the house-fly  
*Musca domestica*.

NASEER-UD-DIN.

In this paper are given the results of experiments concerning the effects of temperature and humidity on the eggs, larvæ and pupæ of the house-fly *Musca domestica*.

It has been found that 35°C. is the optimum for pupal formation, as at this temperature all the larvæ underwent pupation. 6°C. and 45°C. are the minimum and maximum temperatures for the larvæ. No emergence of flies takes place at 40°C. or above.

70% humidity seems to be the optimum for pupation and emergence of flies.

21. Observations on some factors governing the emergence  
of Anopheline mosquitoes.

P. SEN, Calcutta.

The actual processes involved in the emergence of adult mosquitoes from the pupal stage have been detailed in this paper. The hours of the day favoured for emergence by the various species of Anophelines together with some instances of daily fluctuations in the hours are given. The time required for this act varied considerably in the different species; altogether ten species have been considered. The effect of light and temperature on the emergence of mosquitoes are also dealt with. The study proved that a spontaneous control is maintained over the species during this transforming period through structural deficiency and malformations of locomotory organs, or through the activities of different parasites and predatory bodies.

22. A note on the occurrence of a style-sac in some more  
Gastropod genera.

R. V. SESHAIYA, Annamalainagar.

Dr. Yonge has recently made a list of forty-one Gastropod genera in which the style-sac has been recorded till now. From this list *Ampullaria* will have to be deleted, since Bouvier's observation on the occurrence of a style-sac in its stomach has not been confirmed by Dr. Prashad's investigation.

The present note records the presence of a style-sac in two more Gastropod genera, viz. (1) the fresh-water *Septaria* (Neritidæ), and (2) the terrestrial *Cyclotopsis* (Pomatiidæ).

In both the genera the style-sac communicates by its entire length with the intestine; but in *Septaria* the communication is wide and open, while in *Cyclotopsis* it is restricted or narrow.

23. Preliminary observations on the life-history of *Gobius*  
*neilli* Day.

R. GOPALA AIYAR, Madras.

The paper deals with the early stages of development after fertilization.



After fertilization the outer cover of the egg swells out into a club-shaped structure. The micropyle comes to be placed at the narrow end of the club through which mucilaginous threads flow out and anchor the egg-case to the substratum. The case itself is packed with a jelly-like material in the centre of which the embryo undergoes its development.

Early stages of development are described. The embryo is almost fully formed 24 hours after fertilization. The head, eye vesicles, brain, and notochord are established.

The details of development during the second and third day after fertilization are also given. Hatching takes place just before the commencement of the third day. Methods of hatching and further details of the free swimming larva are described.

## 24. On the structure of the pyloric cæca in the Family Ophiocephalidæ.

M. RAHIMULLAH, Hyderabad (Deccan).

Four species, viz. *Ophiocephalus marulius*, *O. striatus*, *O. punctatus*, and *O. gachua* have been investigated. Two cæca are given off just at the commencement of the small intestine.

The cæca in these fishes are two tubular outgrowths of the intestine and vary considerably in size in relation to the alimentary canal, and they also differ very much in form and arrangement in other teleostean fishes. As a rule, in the Ophiocephalidæ, the right cæcum is always smaller than the left.

The cæca are true outgrowths of the intestine as has been corroborated by their histological character. Each cæcum is more or less a finger-like structure, and may be tapering to a point as in *O. marulius* and *O. striatus*, or club-shaped in *O. punctatus*, or slightly pointed in *O. gachua*, and communicates with the intestine by means of an orifice not guarded by any sphincter muscles like those present at the posterior end of the pylorus. On average the ratios of the length of the cæcum to the intestine as well as to the total length of the whole of the alimentary canal in *O. marulius*, *O. striatus*, *O. punctatus*, and *O. gachua* are

$$\frac{1 : 6.2}{1 : 5.2} \text{ and } \frac{1 : 8.7}{1 : 7.3}, \frac{1 : 3.9}{1 : 3.2} \text{ and } \frac{1 : 5.2}{1 : 4.2}, \frac{1 : 6.6}{1 : 4.8} \text{ and } \frac{1 : 8.6}{1 : 6.2}, \text{ and} \\ \frac{1 : 7.1}{1 : 5.7} \text{ and } \frac{1 : 8.5}{1 : 6.8}$$

respectively (in each case the numerator denoting the right cæcum and the denominator the left cæcum).

Their blood- and nerve-supplies have also been recorded.

The histological details of the whole of the gastro-intestinal tract have been carefully studied in each of these species.

These pyloric cæca may tentatively be regarded, in view of their morphological and histological characters, as accessory food-reservoirs, supplementing probably both digestive as well as absorptive functions. Bile and liquid food (deep brown in colour) have invariably been observed to fill their cavities.

## 25. On the bionomics, structure, and mode of intestinal respiration in certain loaches obtained from the Nizam's dominions.

B. K. DAS, Hyderabad (Deccan).

Two types of loaches found in Southern India have been investigated, both being usually confined to the shallow corners of the rivers



away from the main current, and are less frequently met with in ponds or tanks. Breeding takes place during the first showers of rains (May-June); the eggs are laid in the shallow part of the river where dirty water collects, and the larvæ hatch out in about three weeks' time. They are quite abundant during the winter, but only a few are seen during the summer, when, if the mud or sand dries up superficially, they bury themselves completely in the wet mud below and æstivate, lying in a torpid condition, until the rains set in and resuscitate them from their 'summer sleep'. They often prefer to lie buried in the sand or mud, usually with the head and the tail-fin (sometimes this also might disappear from sight completely) peeping out of the substratum. In this position they would remain from half an hour to 2 or 3 hours.

The fish adopts both the *branchial as well as intestinal modes of respiration*, the gill-breathing is extremely fast and goes on very vigorously, on average 238 oscillations per minute. In dirty water (containing very little O<sub>2</sub>) branchial respiration is practically suspended, and in its place the intestine serves as an accessory organ of breathing, and under such circumstances it could survive for at least 72 hours. Under normal conditions in clean water, however, it occasionally (intervals varying from 2 to 5 minutes, or even less according to the temperature and the O<sub>2</sub>- and the CO<sub>2</sub>-contents of the water) darts off to the surface (often popping nearly  $\frac{1}{3}$  or  $\frac{1}{2}$  of the anterior part of its body), opens its mouth and takes a gulp of air very quickly, and immediately after it makes a complete somersault, and at the same time driving out the used up gas from its intestine through the anus (8-12 bubbles) with such an energetic force as to produce a distinct sound. A peculiar kind of clink is also invariably heard when the fish is taken out of water and handled on the ground due to the same cause.

Intestinal respiration is known to occur among loaches, the best known example being *Misgurnus fossilis*. Dobson described this phenomenon in the case of the Indian loach, *Lepidocephalichthys balgara*. The author has described the results of experiments on the asphyxiation of the above-mentioned species. The behaviour of these fishes to perfectly dry conditions is also indicated. The internal structure, nerve- and blood-supply of the alimentary canal are also discussed.

The internal structure, blood- as well as the nerve-supplies of the alimentary canal are also discussed.

## 26. A statistical study of growth in *Therapon jarbua* Day.

S. RANGA RAO, Madras.

It is found that the first yearlings live in the brackish waters of the Adyar and Cooum rivers and the second in the open sea.

Observations on the condition of the gonad and the spawning season seem to indicate that the first yearlings pass into the sea to attain sexual maturity.

A representative collection of specimens was made from October '32 to September '33. The rate of growth for each month is deduced from frequency graphs. The lengths for age in months are also tabulated.

There is reason to think that the rate of growth of the second yearlings is greater than that of the first, probably due to the change from brackish water to open sea conditions.

It is noted that the rate of growth is above average during the cold months December and January, average from January to March and below average during summer, i.e. from April to July. It is suggested that the quantity of food available in various months must be responsible for the fluctuations in growth.



27. The phasical morphology of the thymus gland in some common European fishes and in two Cyclostomes.

S. H. LELE, Bombay.

This paper is a continuation of the author's paper 'On the phasical history of the thymus gland in plaice of various ages', etc., published in the *Journal of the University of Bombay*, Vol. 1, pt. V. It has been thought so far that the thymus gland disappeared or became reduced to a vestige in fishes at or about the time of their maturity. This investigation has shown that this is true only in the case of some fishes like Dogfish, Herring, and Trout. In the case of flat-fishes and rays, on the contrary, the thymus is found to grow even after their reaching maturity.

28. On the variations in the arterial system of the common Indian bull-frog, *Rana tigrina*.

N. K. SINGH, Agra.

In *Rana tigrina* there are considerable individual variations in the arteries. Mostly these variations are graded. They cannot be interpreted as abnormalities and they have not so far been mentioned.

The author has indicated the various ways in which the cardiac, the musculo-glandularis, the œsophageal arteries arise. The relationship of the subclavian artery of each side with the branchial nerve is given. It is shown that the urinogenital arteries vary in number and supply, the posterior lumbar arteries are very variable in their origin, the posterior mesenteric artery varies considerably from its normal position and besides these individual variations several other abnormalities were observed by the author and are described in detail.

29. A contribution to the study of the plankton in the Bombay harbour.

S. H. LELE and (MISS) P. B. GAE, Bombay.

The present paper is based on the samples of the surface plankton of the Bombay harbour collected at least once a week during the year 1932-33. This work has shown that there are cyclic changes in the quantities of daily catches made under constant conditions and the influence of the various physical factors connected with these changes is discussed in this paper.

A superficial examination of these planktonic catches has shown that the macro-organisms in these catches fall into three chief categories. The first consists of animals like *Sagitta* spp. which are found throughout the year in varying quantities. The second consists of organisms as fish eggs and fish and crustacean larvæ which lead planktonic life and appear for short periods. The crustacean larvæ, when present, form the major part of the catch. To the third category belong organisms like siphon-, hydro-, and scypho-medusæ, diatoms, and dinoflagellates which are planktonic throughout their lives but which appear in the Bombay creek for short times at intervals. When present they appear in swarms, thereby increasing the quantity of the catch and appearing to monopolize the whole of the habitat.

Further work is being carried on.

30. The mechanism of the posterior limb of the climbing Marsupials.

B. M. LAL, Hyderabad (Deccan).

In this paper, the author has endeavoured to show that there is more extensive movement in the posterior limb of the Marsupials than



lead wholly or partly an arboreal life, than in the posterior limb of the terrestrial Marsupials or in Eutheria. The posterior limb of the climbing Marsupials resembles the anterior limb in many respects. The joints between the two bones of the leg permit a limited amount of pronation and supination. These movements are effected by the tibio-fibular interosseous muscle and by Pronator Tibiæ or M. Popliteus, which in these animals functions as a pronator muscle on account of its origin from the fibula. The influence of habit on the posterior limb of the climbing Marsupials is discussed. The muscles of the posterior limb of the entirely arboreal and slow moving *Didelphys* are comparatively much weaker, and its bones comparatively much longer and more slender than those of the partly arboreal and partly cursorial *Dasyurus Viverrinus* or those of the partly saltatorial and partly arboreal *Dendrolagus*. It is also pointed out that structurally the foot of *Didelphys* is most primitive, and resembles the hand of quadrumana or man.

### 31. On the development of the vertebral-centra of the vertebrates.

H. K. MOOKERJEE, Calcutta.

Contrary to the opinion of the previous authors, the writer holds the view that the different vertebrates follow a general basic principle in the formation of the vertebral-centra. After the formation of the notochord and its sheaths, the skeleto genous layer aggregates round them forming an outer jacket known as the perichordal tube. In the vertebral region, in some cases, the perichordal tube is very thin, in consequence of which, perhaps, the previous workers thought that the arcualia (dorsal or ventral arches) directly sit on the notochordal sheaths. The perichordal tube then becomes osseous in the vertebral zones. Intervertebral portions of the perichordal tube remain membranous or procartilaginous for a long time. Through these intervertebral zones of the perichordal tube the migratory connective tissue cells pass in. In a procœlous vertebra as in Anura, in some Lacertilia, Ophidia and in some Chelonia, the direction of the migratory connective tissue cells is cranio-caudal, while in the case of a ophisthocœlous vertebra as in higher Urodela, some Anura, and some Chelonia, the direction is reverse of what has been stated. These migratory connective tissue cells cut the intervertebral zones of the perichordal tube into two portions, and the synovial cavity is formed between these portions. The formation of the intervertebral synovial cavity starts from the periphery and not from the centre of the intervertebral element as described by the previous authors. The anterior portion of the intervertebral zone of the perichordal tube goes to form the posterior part of the preceding vertebral centrum by fusion, and the posterior half of the intervertebral zone constitutes the anterior part of the next vertebral centrum. In the case of amphicœlous vertebra, the migratory connective tissue cells instead of getting in through the membranous intervertebral zones, aggregate round them so as to form three bands, one behind the other. The middle band is responsible, either, for the formation of the intervertebral ligament as in fishes, lower Urodela, some reptiles and in birds, or for the formation of the intervertebral disc as in mammals. The lateral bands ultimately become cartilaginous forming the two surfaces of the vertebral-centrum. So that neither the notochord nor its sheaths play any part in the formation of the intervertebral ligament, although that is the opinion of the previous workers.

### 32. Preliminary study of the embryology of *Wallago attu*.

NAZIR AHMAD.

The ripe egg of *Wallago attu* possesses a germinal-disc before fertilization. The endoderm is formed by the invagination of the margin of



the blastoderm within five hours after fertilization. The segmentation-cavity lies between the two primary germ-layers. The mesoderm makes its appearance as two lateral bands, which are thickest at the Kupffer's vesicle and gradually become thinner towards the anterior end. The notochord also becomes manifest in the region of the Kupffer's vesicle, and arises from the endoderm. In *Wallago attu*, as in other Teleosts, the archenteric cavity is absent, the alimentary canal arising as a solid structure.

### 33. Cytoplasmic inclusions in the oogenesis of *Gobius neilli* Day.

M. K. SUBRAMANIAM and R. GOPALA AIYAR, Madras.

The cytoplasmic inclusions were studied from fixed material as well as *intra vitam*.

The mitochondria occur as a dense cloud of granules immediately surrounding the nucleus. With the growth of the oocyte they were seen to move almost in the form of a ring away from the nucleus leaving a fairly clear space round the nucleus. They multiply quickly and soon occupy the whole area of the cytoplasm. They are not observed to take part in deutoplasmogenesis.

The Golgi apparatus occurs as an irregular mass just touching the nuclear membrane. This breaks up and moves into the surrounding cytoplasm in the form of granules. Later they seem to be associated with fatty yolk globules.

Fat and fatty yolk both occur in the egg. Fat seems to arise from nucleolar extrusions. Fatty yolk probably arises by condensation of material by the Golgi apparatus.

### 34. Cytoplasmic inclusions in the oogenesis of *Clibanarius olivaceus* Henderson.

M. K. SUBRAMANIAM, Madras.

A description of the cytoplasmic inclusions in *Clibanarius* leading to the formation of albuminous and fatty yolk grains is given. The mitochondria which occur in the youngest oocytes as a circumnuclear nebulous cloud resolve themselves into definite granules and form a concentration below the cell membrane at one pole of the egg. Masses of mitochondria clump together and these clumps, in association with Golgi batonettes, seem to give rise to albuminous yolk grains.

Fatty yolk is formed by the enlargement of Golgi elements into Golgi vacuoles with subsequent condensation of fatty yolk material in their interior.

A seasonal change was observed and it was found that when the river bar was open the eggs were small and contained large numbers of fatty yolk droplets. In summer when the bar was closed the oocytes were larger in size and contained more of albuminous yolk grains and less fatty yolk droplets than during the former period. The unmodified Golgi elements in this series of preparations were observed to clump together and give rise to albuminous yolk grains in association with Golgi batonettes.

The cytoplasmic substances synthesized by the nucleolus are sent out as extrusions and these seem to be condensed by the Golgi batonettes and utilized in the formation of both kinds of albuminous yolk grains.



# INDIAN SCIENCE CONGRESS.

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ABSTRACTS OF PAPERS.

Section of Geology.

*President :—Prof. K. K. Mathur, M.A., B.Sc.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Geology.

### *Abstracts.*

#### 1. Experiments with the Automatic Water-Finder.

N. G. APTE.

In the Bombay Presidency the Agricultural Department has attempted to locate water with the help of the Water-Finding machine designed by one Mr. Schmidt and manufactured by Messrs. Mansfield & Co., Liverpool. The working of the machine depends upon the vertical earth currents according to the manufacturers. According to the instructions that are sent with the machine it should work for about eight hours in the day. The design of the machine is very simple. It has two chambers; the lower one is sealed and it contains a steel wire coil wound round a spindle. In the above chamber is a pivot on which the magnetic needle is placed while working the machine. It is by the oscillations of this needle that the quantity of water is estimated. It is only in the mornings that the machine gives reliable results. A heated soil also affects the working. The machine has got its limitations and has to be worked with due caution. The successful working needs a well-trained operator who can differentiate between the movements due to an underground current or otherwise, as many times certain factors that affect the working escape notice of even a cautious worker. Besides he has to be well-trained in the Geology of Water Supplies so that he can approximately fix the water-bearing locality.

#### 2. Reflexions on some aspects of the Geology of Bombay.

JAYME RIBEIRO.

The author after reviewing the facts as observed or ascertained by him comes to the following conclusions:—

1. (a) That six of the original seven islets which form the nucleus of the present Island of Bombay owe their origin to a sudden subsidence of the surrounding land;

(b) That this event took place after the volcanic activity that gave rise to the traps and breccias had ceased;

(c) That subsequent to this there have been some slight rises and falls in the levels of Bombay;

(d) That the seventh islet, Mahim, is a sand bank.

2. That the jasperised rock of Antop Hill was emitted from a crack in the crust extending from the south end of the harbour to Antop Hill in the north.

3. (a) That the sedimentary beds of Worli-Camballa-Malabar Hills were deposited by a river which flowed from the north, at a time when the coast line was far away;

(b) That the sea approached the beds by the probable subsidence of a vast tract of land on the west subsequent to the outburst of scoriaceous trap and prior to the basaltic lava flow;

(c) That the sea partially covered the beds owing to the later dip of  $15^{\circ}$  to the west;

(d) That the other fresh water deposits took place in lagoons earlier than the Worli beds.

4. That the scoriaceous trap issued from three parallel cracks in the ground giving rise to (a) Malabar-Worli-Bandra Hills, (b) Sewri-Golanji-Rowli Hills, (c) Nowroji-Sewri Cemetery Hills.



5. That the basaltic trap issued from a point where the harbour now is, or a little beyond it, in a north-westerly direction.

### 3. Notes on the Geology of the Lower Cuddapahs.

C. PRASANNAKUMAR and M. R. SRINIVASA RAO.

As a result of a recent detailed study of the Lower Cuddapahs in the field, several interesting facts have been noticed and these are briefly described in the paper. Special attention is drawn to the stratigraphical position of the included traps, and from their behaviour towards the adjacent rocks, the exact character of these trap flows is discussed.

### 4. Probable horizon of the Nandikonda-Chintalpalem Conglomerates in relation to the associated quartzites.

L. S. KRISHNAMURTHY and C. MAHADEVAN, Hyderabad.

Between Nandikonda (Lat.  $16^{\circ} 35'$ ; Long.  $79^{\circ} 18'$ ) and Chintalpalem (Lat.  $16^{\circ} 35'$ ; Long.  $79^{\circ} 23'$ ) in Nalgonda District H.E.H. the Nizam's Dominions, along the north bank of the Krishna river, some beds of conglomerates have been noted in association with quartzites. Due to want of adequate stratigraphical evidence, the age of these beds with the associated quartzites has not been clearly defined.

The paper describes the petrological characters of the various pebbles and the matrix constituting the conglomerate, and discusses the probable horizon of the formation, in relation to the occurrence of old diamond mines in the neighbourhood.

### 5. Detailed Stratigraphy of the Jumara Area, Cutch.

RAJ NATH, Benares.

The author mapped parts of western Cutch on a scale of  $1''=1$  mile in the year 1927 showing the outcrops of the series of Patcham, Chari, Katrol, and Umia separately. An area in the western region of Cutch and near the village of Jumara was mapped in greater detail on a scale of  $4''=1$  mile. The Patcham and the Chari Series were sub-divided into 26 divisions and fossil collections were separately made from each. These beds form a denuded dome and show a beautiful set of radial dip-faults. There are minor igneous intrusions in the area affecting these beds.

### 6. Detailed Stratigraphy of the Nari beds west of Bagatora Railway Station, Sind.

K. K. MATHUR, G. W. CHIPLONKER, and M. L. MISRA, Benares.

The area west of Bagatora ( $26^{\circ} 21'$ ,  $67^{\circ} 55'$ ) was visited and a large collection of fossils was made bed by bed from the Nari formation. It was also mapped on the scale of  $1''=1$  mile. The Kirthar limestone forms the exposed base of a dome and is succeeded on the west by scarps of Lower Nari, unfossiliferous Upper Nari (or Gaj) and the Manchhars. Blown sand and alluvium cover large tracts on all sides. The Lower Nari Series which consists of thin limestone beds interstratified with thick variously coloured shales, is divided into four zones, the fourth being further divided into five sub-zones. This zonal division of the Lower Nari Series in the field is supported by the palaeontological study of gastropods and nummulites.



## 7. Notes on the Geology of Vengurla. II.

K. V. KELKAR and P. K. LOHOGAONKAR, Poona.

The paper includes supplementary notes on the Geology of Vengurla, results of chemical analyses and a map of the area on a scale of 1" to a mile.

## 8. Notes on the occurrence of ferruginous quartzites in the Dharwar rocks of the western part of the Raichur Doab.

H. S. KRISHNAMOORTHY, Hyderabad.

Parallel bands of Ferruginous Quartzites have been noted running in a south-easterly direction from Mudenur (Lat.  $15^{\circ} 53'$  and Long.  $76^{\circ} 18'$ ) to the north bank of the Tungabhadra river, in broken continuity, for a distance of about 40 miles; but they are best developed between Mudenur and Kalmingi (Lat.  $15^{\circ} 43'$  and Long.  $76^{\circ} 32'$ ). They have been found in close association with the chloritic schists of the Dharwar rocks. Several interesting structural features are exhibited by the bands, locally and regionally, and seem to be of the nature of interformational sills in the chloritic bands. The paper discusses their mode of occurrence, structural features, petrological characters and field relations with the other members of the Dharwar Series.

## 9. The Gwalior Trap.

M. P. BAJPAI, Benares.

The trap is exposed at Gwalior, Morar, Barai, Paniar, Chaura, and Mo in the Gwalior State. It occurs in the Morar Series as sills, dykes, and lava flows. There are two types. One is a porphyritic quartz-dolerite containing some biotite. The other is a fine-grained basalt. In both the augite has suffered uralitization. Six chemical analyses show constancy of composition, the average values being silica 50.20, alumina 11.73, ferric oxide 2.01, ferrous oxide 11.94, lime 10.21, magnesia 5.45, soda 4.47, potash 0.94, titania 1.59, phosphorus pentoxide 0.74, manganous oxide 0.49, and water 0.81. The values generally agree with Washington's average for the Deccan Trap except that the Gwalior Trap is somewhat richer in alkalis.

The ferromagnesian minerals were separated from three rocks and analyzed. A comparison of the ratios of magnesia to ferrous oxide shows that the pyroxene is richer than the corresponding rock and supports the view that crystallization enriches the magma in iron contents.

The helium ratios for these rocks determined by Dr. V. S. Dubey give an average of 500 million years which agrees with the Upper pre-Cambrian age of the Gwalior Series.

## 10. Notes on Deccan Trap in Parts of Gulbarga and Osmanabad Districts, Hyderabad State.

C. MAHADEVAN and L. S. KRISHNAMURTHY, Hyderabad.

Parts of Gulbarga and the whole of Osmanabad district are covered with Deccan Trap flows lying mostly in a horizontal disposition. In parts of Osmanabad district, several escarpments, road and railway cuttings, facilitate an accurate study of the nature and sequence of these flows.

The paper describes the field relations and petrological characters of the various Trap flows. Laboratory determination of porosity of type specimens including those from decomposed layers of Trap have been made and these observations incidentally discussed in relation to the water-bearing capacity of the different flows.



# 11. The Outcrop of the Deccan Trap at Jakhmari in Sind, and its Contact-metamorphic Effect.

K. K. MATHUR and BHASKAR RAO VADDADI, Benares.

The trap is a porphyritic medium-grained dolerite, consisting of labradorite, augite, magnetite, and glass, which is yellowish orange in thin sections. The pyroxene has a biaxial angle of  $62^\circ$ . A chemical analysis gave silica 46.24, alumina 14.68, ferric oxide 8.13, ferrous oxide 4.16, titania 1.14, lime 12.04, magnesia 6.62, soda 4.42, potash 0.22, carbon dioxide 0.51, water 2.60, total 100.76. Both in its chemical composition and in the nature of pyroxene it differs from the typical plateau basalt of the Deccan Trap.

It is probably a lava flow and dips towards W  $20^\circ$  S at an angle of  $50^\circ$ . At its bottom occurs a metamorphosed felsite-looking rock with porphyroblastic texture. The recrystallized minerals are albite, anorthite, calcite, some magnetite, and a palagonitic substance. Its composition is silica 40.47, alumina 20.69, ferric oxide 2.40, ferrous oxide 1.29, titania 0.18, lime 20.84, magnesia 1.65, soda 4.92, potash 0.48, carbon dioxide 7.10, water 0.25, total 100.27. It appears that the rock is a calcite-hornfels and has probably resulted from the contact-metamorphism of a calcareous clay.

# 12. Geology of Pavagad Hill.

V. S. DUBEY, Benares.

This hill has previously been studied by W. T. Blanford, L. L. Fermor, and E. J. Beer. Detailed mapping carried out by the author in collaboration with K. K. Mathur shows that rhyolite and basalt are not interbedded. It was originally an isolated terraced hill of basaltic lava flows typical of Deccan Trap. It was intruded by an ultrabasic magma rich in olivine crystals, with which considerable amount of basic tuff was also thrown out. This was followed by the eruption of acid material from several vents giving rise to rhyolite. The turret at the hill top is an intrusive plug and not the remnant of a bed of rhyolite. Flows of rhyolite occur on the surface at all levels showing that this was the last phase of igneous activity and was much later than the Deccan Trap. Complete analyses and petrographic descriptions of basalt, tuff, olivine gabbro, and rhyolite by the author are given in the paper, together with determinations of radio-activity and helium contents. The helium ratio for an acid felsite indicates an age of 5-5.9 million years which corresponds to the Miocene period and indicates an age later than that of the Deccan Trap.

# 13. The Trap of Pali Hill, Bandra, Bombay.

V. R. KHEDKAR, Benares.

The rock is compact and greyish black. The fracture is subconchoidal, and the broken edges are sharp like the Trap of Malabar Hill with which it agrees in all details. A chemical analysis gave silica 51.36, alumina 18.19, ferric oxide 0.17, ferrous oxide 10.80, magnesia 1.11, lime 8.38, soda 4.71, potash 1.09, water 1.82, titania 1.04, phosphorus pentoxide 0.98, manganous oxide 0.17, carbon dioxide 0.09, total 99.94. A thin section shows felt-like laths of felspar in a ground-mass of granular augite, iron ore, and dark brown glass. Olivine is extremely rare. A micrometric analysis gave plagioclase 29.3, augite 20.2, iron ore 9.8, and glass 41.7. Following the nomenclature of Washington the rock may be termed andesine-andesite.



## 14. The Granophyres, Rhyolites, and Trachytes of Western Salsette.

K. K. MATHUR and V. R. KHEDKAR, Benares.

The rocks from this area have previously been studied by M. S. Krishnan, K. K. Mathur and P. R. Jagapathy Naidu. Chemical analyses and micrometric measurements of a large collection made by the author have been carried out. The magmatic relationship of the isolated occurrences are indicated by the following data :—

AREA.	PERCENTAGE OF MODAL QUARTZ BY WEIGHT.	TOTAL SILICA (Average).
(1) Utan and Dongri ..	40.98–49.74	74
(2) Madh and Salsette Fort ..	40.91–43.15	72.5
(3) Kharodivadi and Manori ..	11.48–20.26	62

The authors conclude from the above that the rocks (Granophyres and Rhyolites) of the first two areas are derived from a common source, whereas the rocks of Kharodivadi and Manori are poorer in silica and correspond to granophyric trachyte.

As has been pointed out by previous workers that the lavas of this group flowed out on the coastal plain of marine denudation and appear to be later in age than the Deccan Trap of the Western Ghats.

## 15. A note on the Petrified Palms from Mohgaon Kalan, District Chhindwara, C.P.

K. P. RODE, Benares.

This article deals with a number of specimens of petrified palms collected by the author during the last four years from a small village Mohgaon Kalan in the Chhindwara District, C.P. In two previous articles the author has described in detail the anatomical characters of three new species of fossil palms from this area. In the present article three more species of palm stems have been briefly described from the same collection. They necessitate the creation of the following three new species :—

*Palmoxydon compactum*, *P. mohgaonensis*, and *P. invaginatum*.

There are several specimens of fossil palms still awaiting investigation and are likely to yield some more new species.

All these specimens come from the Upper Cretaceous Intertrappean Beds.

16. On *Rhizopalmoxydon penchiensis* sp. nov.—a fossil palm root from Mohgaon Kalan, District Chhindwara, C.P.

K. P. RODE, Benares.

The specimen described in this article was collected by the author along with a large number of petrified angiospermous plants from the above locality.

Of the few root types obtained from this area the one described here is the most abundant and conspicuous. The preservation in silica is excellent giving the minutest details under the microscope. The type of anatomy observed in the specimen is essentially the same as that in the living representatives of the palm family. As this find is almost the first of its kind in India comparison with other fossil palm roots from this country is not possible. The author has attempted a comparison with the few fossil palm roots described from other countries, as also with the numerous types of roots of the living palms. The specimen is



assigned to the form genus *Rhizopalmoxylon*, Felix, while the specific name is from the important river Pench flowing close by. The specimen belongs to the Intertrappean beds of Upper Cretaceous age.

17. A note on a Fossil Dicotyledonous Wood from Mohgaon Kalan, District Chhindwara, C.P.

K. P. RODE, Benares.

In this article the author has briefly described the anatomy of one of the several specimens of fossil dicotyledonous wood collected from the intertrappean rocks of Mohgaon Kalan. The specimen described here is characterised by medullary rays, mostly one cell thick, separating groups of large wood vessels which are very commonly in pairs. The annual rings, though present, are not conspicuously marked off under high magnification.

The author in attempting to compare the anatomical details of this wood has noted the extreme difficulty of such a comparison in the absence of any regular scheme of classification of dicotyledonous plants on the anatomical basis. Of the few dicotyledonous plants having medullary rays one cell thick the nearest approach, so far as the author is aware, appears to be *Juglans*. The author has therefore provisionally named the fossil wood as *Parajugloxylon mohgaonensis* suggesting thereby not the generic identity with *Juglans* but its close approach.

18. Palæontological Study of Nummulites from the Laki Dome and the Hills near Bagatora, Sind.

RAJ NATH and M. L. MISRA, Benares.

During the course of the field work when a zonal sub-division of the Lower Nari was being attempted, a large collection of fossils was made bed by bed from areas west of Laki ( $26^{\circ} 16'$ ,  $67^{\circ} 57'$ ) and Bagatora ( $26^{\circ} 21'$ ,  $67^{\circ} 55'$ ). The palæontological results based on the study of the nummulites support the proposed division of the Lower Nari Series into four zones, and the further division of the fourth zone into five sub-zones. These divisions are characterised either by certain restricted species or by a suite of species.

19. On a fossiliferous quartzite from the Trichinopoly Cretaceous.

L. RAMA RAO and C. PRASANNAKUMAR.

The paper describes a fossiliferous quartzite from the Trichinopoly Cretaceous. In micro-sections the rock is a typical quartzite, showing a regular mosaic of quartz grains. Corals like *Heliastrea*, *Holocænia*, a few foraminifers of the family Miliolidae, and abundant algæ—chiefly *Lithothamnion*—are the common fossils. The rock must originally have been a fossiliferous sandstone, subsequently silicified. Such a secondary fossiliferous quartzite is a very unusual type of rock and is therefore of interest.

20. Rhynchonellids from the Bagh Beds near Cheerakhan, Gwalior State.

RAJ NATH and CHIPLONKAR, Benares.

The Bagh beds, constituting the marine facies of the Cretaceous of the Narbada valley, have, ever since their discovery by Col. Keatinge in 1856, been a subject of considerable interest because of the faunal



contrast they present to the Trichinopoly Cretaceous. So far echinoids and ammonites have been described from the Bagh beds and on the basis of the echinoids Duncan has assigned the Cenomanian age to this formation. The authors describe a Rhynchonellid fauna from these beds, which is characterised by fine acute ribbing regularly developed, a hypothyrid to sub-mesothyrid collared foramen, pear-shaped muscle-areas and weak dorsal medium septum. These characters indicate a Cretaceous age.

## 21. Revision of the Jurassic Brachiopod Fauna of Cutch.

RAJ NATH, Benares.

The author, during his field work in the year 1927, made a large collection of Brachiopod fauna along with other invertebrate fossils from the Jurassic beds of Cutch. The last detailed investigation of the brachiopods from this area was made by Dr. Kitchin in the year 1900. In view of the recent advances in our knowledge of the brachiopod group made since then, the author thought it necessary to undertake a revision of this fauna. The important results of this investigation, embodied in this paper, are :—

- (1) the creation of four new species (*Lobothyris soorkaensis*, *Lobothyris* ? *patchamensis*, *L.* ? *kitchini*, and *Streptorhynchus* ? *jumarensis*),
- (2) a revision of the geological range of certain species,
- (3) possible extension of the *Productus* beds of the Salt Range to some parts of Cutch deduced from the occurrence of a derived Palæozoic form in the Jurassic beds.

## 22. Palæontological Study of Gastropods from the Laki Dome and the Hills near Bagatora, Sind.

RAJ NATH and G. W. CHIPLONKAR, Benares.

While working out the zonal sub-divisions of the Lower Nari, an extensive collection of fossils was made from areas west of Laki ( $26^{\circ} 16'$ ,  $67^{\circ} 57'$ ) and Bagatora ( $26^{\circ} 21'$ ,  $67^{\circ} 55'$ ). The gastropods from this collection were taken up for palæontological study. As the collection was made bed by bed, it has been possible to study the vertical distribution of the species; as a result of such work the Lower Nari Series is divided into four zones, the uppermost of which is further divided into five sub-zones; so that palæontological results are in agreement with the field evidence. The study of nummulites also support these results.

## 23. A New Species of *Oxyglossus* from the Frog-Beds of Warli Hill, Bombay Island.

G. W. CHIPLONKAR, Benares.

The small frogs from the Frog-Beds of Bombay Island have long since been known as *Oxyglossus pusillus* (Owen). A recent collection of these fossil frogs from the Frog-Beds of Warli Hill, on the west coast of Bombay Island, has revealed a new species of frogs occurring associated with *Oxy. pusillus* (Owen). It probably attained a slightly bigger size than *Oxy. pusillus* (Owen); the length of the head is a little less than the width; the sacral vertebra, including ilia and ischia, is more than two-thirds of the vertebral column and the posterior limbs are one and two-thirds times longer than the body. Other associated fossils are minute Crustaceans and carbonised vegetation.



24. On a Stegosaurian humerus from the Lameta beds of Jubbulpore.

D. K. CHAKRAVARTI, Benares.

The author describes the left humerus of a Stegosaurian dinosaur, which was collected by him from near the junction of the mottled nodular beds with the upper limestone exposed on top of the Chota Simla hill at Jubbulpore. No other humerus of any other orthopodous (ornithischian) dinosaur has yet been found in India. The present find is therefore of considerable interest.

The humerus described cannot be assigned to the only known Indian orthopod, *Lametasaurus indicus*, in the absence of any humerus found for the latter. On the other hand, considering the small size of the present bone and the fact that it has been found on a horizon which is sixty feet or more above the horizon of *L. indicus*, it may be regarded as belonging to a different species and perhaps to a different genus.

25. A study of Equine Molar Teeth from the Older Gangetic Alluvium of Benares.

D. K. CHAKRAVARTI and BHASKARA RAO VADDADI, Benares.

The authors describe two equine teeth, one the first left lower molar and the other the first right lower molar, obtained from the Older Gangetic Alluvium in the District of Benares. No equine molars have yet been reported from the same formation. This justifies a detailed study of these teeth. After comparing the present teeth with all the available homologous teeth described or figured, or exhibited in the Indian Museum in Calcutta, the authors come to the conclusion that one of these shows strong affinity with a specimen of *Equus namadicus*, and that the other appears to be a new species.

26. On the systematic position of *Lametasaurus indicus*.

D. K. CHAKRAVARTI, Benares.

The name *Lametasaurus indicus* was provisionally proposed by Dr. Matley for the so-called Indian Stegosaurian, which is represented by a sacrum, a pair of ilia, a left tibia, two lateral spines and many scutes. Later, a number of tabular scutes and a terminal caudal plate were also known. According to Dr. Matley this Indian specimen approaches the genus *Omosaurus* in most respects. This latter genus closely resemble *Stegosaurus*, and as such *L. indicus* has been placed by Dr. Matley in the family Stegosauridæ. But in the second revised English edition (1932) of Zittel's text-book of Palæontology, Vol. II, it has been provisionally placed in the family Nodosauridæ. This is perhaps due to the fact that the tabular scutes resemble those of *Palæoscincus*, other scutes and spines those of *Polacanthus* and the terminal caudal plate that of *Ankylosaurus*—all these three genera coming in Nodosauridæ.

The present author points out that the tibia referred to *L. indicus* cannot belong to a Stegosaur or a Nodosaur, because, unlike the latter two the former has got the greatest diameters of the expanded extremities lying nearly at right angles to one another—a character to be found in the Ceratopsidæ and *Camptosaurus*. This necessitates the separation of the tibia from the material, the rest of which may be assigned to the same species and placed in the Nodosauridæ with greater certainty.



27. Auriferous quartz in the Dharwar Rocks of the Raichur Doab.

S. K. MUKERJI, Hyderabad.

Auriferous quartz reefs and veins in the Dharwar rocks of the Raichur Doab, have long been noted as evidenced by numerous scattered old gold-workings. The Geological Survey of H.E.H. the Nizam's Government directed their attention to this occurrence with a view to obtain an intimate knowledge of the geology of the area from an economic point of view.


The paper gives a summary of the salient geological factors bearing on the occurrence of gold in relation to the hornblende schists and the associated gneisses. The peripheral distribution of the old gold workings in the schists in proximity to the gneisses, the blue quartz reefs and their relation to the Dharwar schists and to the gneisses, especially at their contact with the schists, are discussed.

28. The manufacture of refractories from Indian magnesite.

H. K. MITRA, Jamshedpur.

Deposits of very pure magnesite found in the Mysore State and owned by the Tata Iron and Steel Company are used in the manufacture of refractories at Jamshedpur. The two forms in which this refractory material is used are (1) 'pea' size magnesite, and (2) Brick. The first stage in the manufacture of either of these varieties is the 'dead-burning' of the raw magnesite. The extreme purity of the Indian magnesite compared to that of Austria, which at one time was the only source of magnesite supply, makes the 'dead-burning' of the former difficult. Technical details are given to show how this has been overcome. The 'dead-burning' is accomplished in one process, without any preliminary calcination, in a specially designed gas kiln at a temperature of 1650°C. The dead-burned material is then crushed and screened to produce 'peas' or else pulverised to a fine powder and molded into brick. The bricks are burned in a rectangular down draft kiln, along with chrome brick. Physical, chemical, and microscopic tests of the magnesite brick are given.

The problem of recovery of carbon dioxide is also discussed.





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ABSTRACTS OF PAPERS.

Section of Zoology.

*President :—Diwan Anand Coomar, M.A.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Zoology.

### Abstracts.

#### 1. Ecological studies of Pink Bollworm (*Platyedra gossypiella* Saunders).

M. AFZAL HUSAIN, M. HAROON KHAN, and NAZIR AHMAD,  
Lyallpur.

The Pink Bollworm is a serious pest of cotton in certain parts of the Punjab and negligible in others. The differences in attack are due to the differences in climate which greatly affect its procreation. The latter is much higher in places of high incidence than in places of low incidence.

It has been established that temperature and humidity acting on both the pupæ and the adults influence egg-laying. The most favourable temperature for the development of gonads and the deposition of eggs lies between 75°F. and 82°F. and of humidity from about 70 to 95%, while the moths emerging from the pupæ kept at 92°F. or above are devoid of fully developed sperms.

The data collected further show that oviposition under natural conditions was highest when the mean maximum temperature acting on the pupæ and the adults was about 90°F., mean minimum 72°F. and the relative humidity 70% or more at 8 hours.

On the basis of these results it is possible to predict the incidence of Pink Bollworm at any place. In places where the pest becomes active at the time of the fruiting of cotton and the climatic conditions are favourable for its oviposition it will be serious but not in others.

#### 2. On the bionomics and distribution of *Herdmania pallida* Lahille (*Rhabdocynthia pallida* Herdman).

S. M. DASS, Lucknow.

The genus *Rhabdocynthia* has, according to the law of priority, been re-named *Herdmania* by the author. It is studied as a type of the Tunicata in almost all Indian Universities instead of the European genera *Ciona* and *Ascidia*. Our knowledge of *Herdmania* has hitherto been very meagre and incomplete; in fact, little work was done on any Indian ascidian since Herdman's visit to Ceylon in 1906.

The following is a summary of the author's investigations into the bionomics and distribution of this typical Indian mon-ascidian:—

The animal is found in the Gulf of Manaar at a depth of 5–12 fathoms, extending as far as 10 miles from the sea-shore. The animal has also been reported from the Indian, Pacific and Atlantic Oceans and from the Malayan Seas and the West Indies.

The bed harbouring *H. pallida* has been called a 'chank-polychæte formation,' as the association between the three animals is almost constant.

It is a solitary animal and is usually found in groups of 10–12 individuals. It remains attached to the substratum by a 'foot' formed by the test; it is often found attached to shells of living chanks (*Turbinella pyrum* and *T. rapa*) and in such cases the association offers a typical example of commensalism.

The food consists mainly of diatoms, algæ, and infusorians.

Besides the constant ciliary water-current passing through the body, the animal takes to voluntary regular contractions of the body and siphons at intervals, which serve as aids to respiration.

*H. pallida* is hermaphrodite and oviparous.



3. On the external characters of *Herdmania pallida*.

S. M. DASS, Lucknow.

A description of the external characters of mon-ascidians is important as in most systems of classification, the external characters form an important criterion for the identification of species.

The following is a summary of the chief characters noted :—

The body is oblong or pear-shaped, about  $9.5 \times 7 \times 4$  cms. in size, with a foot about 3-4 cms. long, which remains imbedded in the sand. The foot is absent when the animal is attached to a hard surface.

The colour of the body is distinctly reddish on account of bright red patches in the test formed by the red-pigmented knobs of the blood-vessels. Herdman's (1891) description of the colour of *H. pallida* has been revised and corrected.

The test is more or less transparent in young animals but usually becomes opaque in the adult.

The branchial and atrial apertures are both 4-lobed, the atrial aperture being almost upright and the branchial always somewhat lateral.

The spinules, on which Lacaze-Duthiers and Delage try to base the identification of species in Cynthidæ, are absent from the external surface of *H. pallida*.

4. On the presence of nerve-cells, nerve-fibres, and receptor-cells in the test of *Herdmania pallida*.

S. M. DASS, Lucknow.

This is the first time that structures comparable to nerve-cells and nerve-fibres have been demonstrated in the test of an ascidian. The general test, and more specially the test of the siphons, is very sensitive and contracts on a slight disturbance of the water in which the animal lies. A pin-prick on the test of any of the two siphons causes an immediate contraction of that siphon. This suggested the possibility of the nervous tissue being present in the test to enable the animal to feel the prick. The nerve-cells and fibres were discovered after staining with methylene blue and methyl-blue eosin. The cells lining the vascular ampullæ, present in the test near its outer surface, have a special supply of fine nerve-fibres and act as receptor-cells. Some receptor-cells are also found scattered in the superficial layers of the test. All the nerve-fibres ultimately join the nerves emerging from the nerve-ganglion.

5. On the mantle and the atrial cavity of *Herdmania pallida*, with a note on the rôle of the muscles in producing movements in the animal.

S. M. DASS, Lucknow.

The mantle of Tunicata, enclosing the large atrial (or peribranchial) cavity, is the body-wall proper of the animal lying just beneath the test. Herdman (1906) gave a short account of the mantle of *H. pallida*, but he makes no mention of the form, structure, arrangement, and particular function of the different sets of muscles.

The results of the present investigation may be summarized as follows :—

The mantle consists of an outer ectoderm of squamous epithelium, a middle layer of parietal mesoderm and an inner ectoderm that lines the atrial cavity.

The outer ectoderm is turned in right down to the base of the 2 siphons forming a stomodæum and a proctodæum.



The muscles of the mantle, confined to the antero-dorsal half of the body, control the different movements of the animal which are described. The muscles can be arranged into (a) the branchial group, (b) the atrial group, and (c) the branchio-atrial group. Besides these a strong sphincter muscle is present at the base of each of the two siphons, which can close the internal siphonal aperture.

The atrial cavity is divided into a right and a left half due to the fusion of the branchial sac with the mantle along the midventral line of the body; but the two halves are continuous dorsally.

6. On the spicules found in the test and the mantle of  
*Herdmania pallida*.

S. M. DASS, Lucknow.

Herdman (1885) gave a description of calcareous spicules in Tunicata and later (1891) founded the genus *Rhabdocynthis* (*Herdmania*) on their presence. He mentions only two types of spicules—the knob-headed and the spindle-shaped varieties. The author has found a third variety—the pipette-shaped spicules—which seems to have been overlooked by Herdman. Mention has been made of the spicules tending to run in ensheathed bundles—a character constant in the last two types of spicules. The spicules are all of the echinated variety.

The spicules have been classified by the author, according to their size, into megascleres and microscleres—the former found in the mantle and walls of blood-vessels and the latter in the test only. The character of the megascleres to pierce almost every organ of the body, except the heart, had not been observed so far.

7. On the neural gland, nerve-ganglion, and dorsal tubercle  
of *Herdmania pallida*.

S. M. DASS, Lucknow.

In both *Ascidia* and *Ciona*, the accounts of which are used in Indian Universities while dissecting the form *Herdmania*, the nerve-ganglion is dorsal to the neural gland, which again is situated dorsally to the ciliated tubercle. But in *Herdmania* it is the neural gland that is dorsalmost, and beneath this lies the nerve-ganglion, a condition reverse of that found in *Ciona* and *Ascidia*. The duct of the neural gland opens by a ciliated funnel at the base of the dorsal tubercle which consists of two spirally-coiled conical projections on a broad base. The structure of the neural gland points to an excretory function, while the ciliation and rich innervation of the dorsal tubercle points to a sensory function of this organ. The relation between the duct of a gland (the neural gland and a pre-pharyngeal sense-organ (the dorsal tubercle) seems to be secondary and purely accidental.

8. On the anatomy and histology of the alimentary canal of  
*Herdmania pallida*, with an account of the digestive  
glands and the method of carbohydrate storage.

S. M. DASS, Lucknow.

The present paper, for the first time, gives a complete account of the gut of a Cynthioid, together with an account of the glands of digestion. The much disputed point of the method of carbohydrate storage in mon-ascidians with a liver, has been discussed.

The tentacles are of four different sizes and about 60 in all and not of three sizes and 32 in number as Herdman (1906) mentioned.



The branchial sac has 10 folds on each side instead of 9 as stated by Herdman. Each stigmatic area has 5-6 stigmata and the animal has about 400,000 stigmata in all.

The dorsal lamina has 20-30 tentacular languets.

The endostyle contains four rows of glandular epithelial cells and a median row of cells with very long cilia.

Orton's conclusions about the mode of feeding in ascidians are confirmed.

The oesophagus has four deep grooves through which the food-laden mucus-thread passes in a spirally coiled state into the stomach. The rectal aperture is bounded by four lips.

The 'liver', consisting of a right and a left lobe, is made up of cæca of a single layer of glandular cells and opens into the stomach by several apertures.

The pyloric gland, consisting of tubules ramifying in the wall of the gut and opening by a single aperture into the mid-intestine, seems to be pancreatic in nature.

Carbohydrate is stored in the form of starch-granules found in the liver and in the stomach wall and to less extent in the walls of the mid-gut and oesophagus.

#### 9. On the blood-vascular system of *Herdmania pallida* with an account of the histology of the blood.

S. M. DASS, Lucknow.

The circulatory system of *Ascidia* was fully described by Herdman in 1899 and that of *Polycarpa* by Lacaze-Duthiers and Delage in 1893. But the blood-vascular system of *Herdmania* differs in several respects from that of *Ascidia*, though it resembles that of *Polycarpa* in certain respects.

The following chief features have been recorded :—

The blood contains 7 different types of corpuscles.

The valvular arrangement in the heart is described.

The ventral aorta, the dorsal aorta, the branchio-visceral vessel and the cardio-visceral vessel are the chief vessels. Definite vessels, supplying blood from the heart to the gut and gonads, are described for the first time as also the origin and distribution of the test vessels.

The course of circulation is briefly described together with an account of the periodical reversal of the course of circulation.

#### 10. On the anatomy and histology of the reproductive system of *Herdmania pallida*.

S. M. DASS, Lucknow.

The genital organs of the Cynthiinae had been worked out in some detail by Lacaze-Duthiers and Delage in 1893. But their observations are mainly on some species of *Cynthia*, *Microcosmus* and *Forbesella*, and the descriptions do not hold good for the genus *Herdmania* which is the fourth member of the sub-family.

The author's findings may be summarized as follows :—

There are two gonads consisting of 10-25 hermaphrodite lobes. Each lobe has a distinct spermatheca and an ovarian region.

Each gonad is provided with a vas-deferens and an oviduct.

At least three types of sperms can be distinguished.

Besides the usual layers the ovum of *H. pallida* has an extra-investing membrane which has been called the inner chorion. This type of egg is described here for the first time in Cynthiinae.

*H. pallida* is protogynous. The genital products pass through the atrial siphon (cloaca) into the sea, where fertilization takes place.



11. On two new Monostomes (Trematoda) from Avian hosts in British India.

G. D. BHALERAO, Muktesar.

Two new Monostomes : *Notocotylus babai* from the cæcum of *Mihus migrans govinda*, Rangoon and *Cyclocœlium shavadi* from the thoracic cavity of *Urocissa favirostris cucullata*, Muktesar, have been described. The new species have been compared with the related species of their respective genera. The affinities of the new species with those allied to them are thoroughly discussed. *N. magniovatus* Yamaguti, 1934, has been regarded as synonym of *N. attenuatus*. A key to all the known species of *Notocotylus* from the avian hosts has been given. The status of the various genera so far included in Cyclocoelidæ has been reviewed.

This is the first occasion on which Monostomes are being recorded from this country.

12. A preliminary note on the nephridia and their funnels in the leech *Hirudinaria*.

M. L. BHATIA, Lucknow.

*Hirudinaria granulosa*, the common Indian leech, is the type dissected in almost all the Universities in India. This leech possesses seventeen pairs of nephridia, metamerically disposed from segments VIII to XXIV, each with a definite external nephridial pore. Hitherto proper attention has not been paid to the structure and disposition of the funnel and preparations made in the laboratories by teachers and students have invariably lacked a funnel. The author has recently been able to make mounts of the funnel from several nephridia in the testicular region. It lies in a blood sinus surrounding a part of each testis. If the dorsal half of a testis sac is mounted, on a slide in a drop of salt solution, from a freshly killed leech, the ciliary movements clearly indicate the presence of the nephridial funnel. The funnel appears as a mass of a large number of horse-shoe shaped cells, which are irregularly arranged and possess rows of cilia upon their free borders. Each horse-shoe shaped cell represents either a separate funnel or probably a lobe of a large crumpled funnel.

13. Gaps in our knowledge of the Indian Protozoa—I. Ciliophora.

B. L. BHATIA, Bombay.

The object of this paper is to survey the Ciliophora so far recorded from different parts of India, and to indicate the provinces from where the records are scanty. Attention is also directed to the families not so far known from India. It is hoped that this will stimulate further research.

14. Gaps in our knowledge of the Indian Protozoa—II. Sporozoa.

B. L. BHATIA, Bombay.

Complete list of the Sporozoa so far recorded from India together with the hosts in which they are known to occur, has been compiled, and it is proposed to publish it later as a check list for the benefit of the medical and veterinary workers and others interested in the subject. Certain gaps in our knowledge of the Sporozoa in India will be pointed out and some problems for future work suggested.



15. On some gregarine parasites from some polychætes from the Andaman Islands.

B. L. BHATIA and S. B. SETNA, Bombay.

One of the authors of this paper (S.B.S.) during a stay of five months in the Andaman Islands examined the gregarine parasites from four polychætes and made a large series of permanent preparations. The hosts are being identified by the Indian Museum authorities.

*Host A.*—Contains in its intestine *Lecudina* sp. very similar to *Lecudina aphroditæ* (Lank.).

*Host B.*—Harbours in its intestine four or possibly five distinct parasites.

(1) *Ulivina* sp., similar to, if not identical with *Ulivina rhynchoboli* (Crawley).

(2) *Stomatophora* sp.—The organism suggests comparison with *Stomatophora simplex* Bhatia, but the sucker has no central mucron.

(3) Septate gregarine. Certain characters re-call the more complete segmentation in *Metamera* and *Tæmiocystis*.

(4) *Contortiocorpa prashadi*, n.g., n.sp.

*Host C.*—Harbours in its coelome *Nematocystis* sp.

16. A note on the origin of the tonofibrillæ in insects as exemplified by a Cecidomyid (Diptera).

P. SEN, Calcutta.

The muscle fibres in this insect at their attachments with the body wall become highly fibrillated. These fibrillations are continued in a converging manner towards the inner border of the dermis. Difference of opinion exists as to the origin of these fibrillæ. Some hold that these are chitinous in structure and originate from the cuticle. Others including Tillyard and Keilin regard them as hypodermal in origin. The present author recently observed that these fibrillæ in the Cecidomyid larvæ are formed by the special secretory activities of the nucleated hypodermal cells at the base. This observation thus supports the views held by the latter school of observers.

17. The Cuckoo-Shrikes of Calcutta.

S. C. LAW, Calcutta.

Three distinct species referable to two genera are noted from environs of Calcutta and contiguous districts. Distribution, status, and movements discussed. Available records meagre or insufficient.

*Lalage m. melaschista* Hodgs.—A winter visitor. Time of arrival and departure. Data available from author's own records. Habits and habitat with reference to migratory area in Lower Bengal described.

*Lalage sykesii* Strickl.—Occurrence in Bengal. Confusion as regards status in its range around Calcutta. Mr. Hugh Whistler's note (The Vernay Survey, J.B.N.H.S., XXXVI, 345) in so far as it mentions this species as 'clearly a rains visitor from about June to September' is erroneous and misleading. Author's observations fairly ample and conclusive, indicating that it is a breeding and resident species. Habitat and nesting area discovered. Young and juvenile coloration described.

*Graucalus macei* Less.—The form found about Calcutta is according to Whistler *Graucalus javensis macei*. Extremely meagre record of its occurrence. Its status discussed and haunts described.



18. A note on the juvenile coloration of some Himalayan birds.

S. C. LAW, Calcutta.

Four species of the Family *Timaliidae* are dealt with, viz. *Stachyridopsis r. ruficeps* Blyth, *Pseudominla c. castaneiceps* (Hodgs.), *Fulveta v. vinipectus* (Hodgs.), and *Ixulus f. flavicollis* (Hodgs.). All collected from Darjeeling and Sikkim. No published record of their juvenile coloration.

19. Observations on the movements of *Dendronanthus indicus* (Gmel.) in the vicinity of Calcutta.

S. C. LAW, Calcutta.

The author's observations regarding this species tend to show that its movements become so pronounced in April and September as to be almost comparable to the migratory movements of some Flycatchers which visit Lower Bengal. Mentioned as winter migrant in both editions of the *Fauna*. Blyth's record 'at all seasons' in the vicinity of Calcutta. Doubt still exists as to its status. No breeding area near Calcutta yet discovered.

20. A note on the variations in the gastric armature of some South Indian Decapod Crustaceans.

A. RAMAKRISHNA REDDY, Annamalainagar.

The gastric armature in six common South Indian Decapods is described. The general plan of the mechanism is the same in all of them; but the structural details especially of the cardiac and urocardiac cuticularizations, the nature of the denticles and the distribution of setæ vary considerably. The variations are apparently correlated with the nature of the food.

The gastric musculature is also varied in correlation with the development and disposition of pylorics and zygocardiacs.

The gastric armature of *Penæus* is peculiar in that six sharp denticles occur dorsally in the œsophagus which may serve for preliminary reduction of food, before it is subjected to the process of straining and mastication.

The gastric armatures present a well graded series of complexities. *Cerataspis montrosus* described by Bonier presents the most primitive type. The gastric armature of *Penæus* is intermediate between this primitive and more advanced types. *Nephrops* and *Astacus* come next in the series followed by Hermit-crabs, *Albunea*, Field-crab and *Gelasimus* in the order of complexity in the gastric armature.

21. On the origin and development of the pharyngeal gland-cells of earthworms.

K. N. BAHL, Lucknow.

In 1917, Stephenson described the microscopic structure of the dorsal pharyngeal thickening in 3 species of *Pheretima* and also in *Helodrilus*. He denied the glandular nature of the pharyngeal bulb and held that the so-called gland-cells are to be looked upon as of peritoneal origin. In 1920, Keilin demonstrated that the pharyngeal dorsal bulb was a true salivary gland. The present paper deals with the origin and development of the gland-cells based on a study of the early embryos of *Pheretima*, *Lampito* (*Megascolex*), and *Eutyphæus*.



22. A note on the anatomy of *Rachisellus prætermisus* Blanford.

R. V. SESHAIYA, Annamalainagar.

The study of the anatomy of *Rachisellus prætermisus* has shown that the radula and reproductive system are strikingly different from that of *Rachisellus punctatus* Anton. The differences are more marked than what may be expected between species of the same genus. In the radula of *Rachisellus prætermisus* the central is large and rounded and the laterals are arranged in oblique series. These are features characteristic not of the genus *Rachisellus*, but of *Rachistia*, a genus recorded till now from South Africa. What has been known as *Rachisellus prætermisus* appears to belong to the genus *Rachistia*.

23. Anatomy of *Melania (Radina) crenulata* (Desh.) var. *tirouri*.

R. V. SESHAIYA, Annamalainagar.

The paper is a study in the comparative anatomy of the Indian Melaniidæ. *Melania crenulata*, var. *confusa* (Dohrn), *Melanoides scabra* (Müller), *Acrostoma baccata*, *Acrostoma reevi*, *Paludomus regulata*, *Paludomus blanfordiana*, *Stomatodon stomatodon* have been examined. The anatomy of *Melania crenulata* is discussed in detail. The reproductive system in *Melania* and *Melanoides* shows interesting features. In the male the lower part of the genital duct is in the form of a wide, partially open furrow. In the female a brood pouch is developed under the mantle floor. The oviduct is a slender duct with a conspicuous receptaculum seminis which opens by a slit-like aperture in close proximity to the opening into the brood pouch. The oviduct joins the receptaculum at its lower end. There is also a very slender duct connecting the upper part of the receptaculum seminis and the oviduct which may be considered as a vestige indicating the origin of the receptaculum seminis from the oviduct. The ova are fertilized in the receptaculum seminis and then pass into the brood pouch where development takes place.

24. Study of biological and ecological conditions of estuarine waters of Bengal and their relation to the malaria problem of the province.

G. C. CHATTERJEE, H. K. MOOKERJEE, and A. N. MITRA, Calcutta.

Fish are recognized as larvivorous. Estuarine waters contain numerous varieties of larvivorous fish. Certain conditions increase their number, other conditions diminish them. These fish live upon various types of crustaceans as well as of protozoa; while in their turn they are eaten up by carnivorous fish as well as by beetles and other organisms present in water.

The study of these ecological conditions offers a great field of study to Biologists and Malariologists. This is the first of the series of observations on this subject.

25. Reproductive system and mating habit of Bruchid beetles.

DURGA D. MUKERJI and M. A. HAKIM BHUYA, Calcutta.

In continuation of previous communications the authors have given in this paper the details of the histology of the genital system of the male and female of *B. quadrimaculatus* and *P. chinensis*. A comparison of the structure of the two species is made. The methods of copulation have been studied in detail and the function of bursa copulatrix is discussed.



26. Comparative study of the digestive system of common ants of Calcutta.

DURGA D. MUKERJI and S. R. MAZUMDAR,  
Calcutta.

The alimentary canal of the species commonly found in Calcutta representing sub-families—Ponerinae, Myrmecinae, and Camponotinae—is investigated. A comparison is made between gizzard of the nearly related species of the genus *Camponotus* which contains species with a highly variable structure. Attempt is also made to find out correlation between feeding habits and the structure of the gut.

27. On the morphology of *Chilomitus caviæ*, a flagellate from the coecum of guinea-pig.

H. N. RAY and A. N. MITRA, Calcutta.

Morphology of this flagellate has been described in detail. Presence of an internal axoneme arising from one of the basal granules has been definitely established. Its method of division has also been studied in some detail. Similar flagellates from rats and toads are also reported.

28. On the species of *Stenophora*—a septate gregarine, from an Indian millepede, *Cambalopsis* sp.

H. N. RAY and M. CHAKRAVORTI, Calcutta.

Morphology and life-history of this gregarine are described in detail. A discussion follows on its intracellular habit and method of movement. A method for obtaining cysts of gregarines from millipedes is also given.

29. On a species of *Eimeria* (Sporozoa-coccidia) from the gall-bladder of a lizard, *Hemidactylus coctæi*.

H. N. RAY and M. DAS GUPTA, Calcutta.

This coccidian has been shown to be entirely confined to the epithelium of the gall-bladder of Lizard and that none of the stages in its life-history is passed through the liver or intestine of the host as has been pointed out by another worker. Intestinal epithelium, no doubt, contains a species of *Eimeria*, but it has been found to be quite different from the one in question. Life-history of this *Eimeria* has been described in detail. Unlike *E. perforans* mature oöcysts are found in the faecal matter.

30. On a new species of *Eimeria* (Sporozoa-coccidia) from the intestine of toad, *Bufo melanostictus*.

H. N. RAY, Calcutta.

Morphological peculiarities such as occurrence of a pair of hyaline blades at the anterior end of merozoites, young trophozoites and schizonts and situation of the fertilization spindle at right-angles to the long axis of the macrogametes have been discussed. Two types of schizogony have been described, microschizogony which ultimately gives rise to microgametes, and macroschizogony which gives rise to macrogametes. Schizogony has been found to commence at a very early stage—even before a merozoite has become intracellular. Sporogony is rigidly intracellular.



31. Cause leading to the formation of different forms of vertebræ.

H. K. MOOKERJEE, Calcutta.

In vertebrata we generally find four forms of vertebræ, namely procœlous, opisthocœlous, amphicœlous and heterocœlous. The intervertebral portions of the perichordal tube remain membranous or procartilaginous for a long time. Through these intervertebral zones of perichordal tube, the migratory connective tissue cells enter. The mode of entrance of the migratory connective tissue cells depends on the habit of the embryo. When the embryo oscillates its body except the head, we get the procœlous type. Oscillation towards the opposite direction produces the opisthocœlous type. When the embryo does not flex its body we get the amphicœlous form. Heterocœlous type is the modified form of procœlous.

32. Position of the cartilaginous neural arch in the thoracic vertebra of chelonia.

H. K. MOOKERJEE and A. K. MUKHERJEE,  
Calcutta.

Previous workers were of opinion that the position of the basidorsals were at the intervertebral region of the thoracic vertebræ, but our recent investigation disproves their observations. They are really at the vertebral region and between the two consecutive cartilaginous arches there is a connective tissue arch to fill up the gap.

33. On the development of the vertebral column of snake.

H. K. MOOKERJEE and B. K. CHATTERJEE, Calcutta.

The authors have traced the development of the vertebral column of snake. They differ from the previous workers on the constant parts of the upper arch throughout the whole vertebral column and the lower arches at the tail region.

34. Genitourinary system of *Sciurus* (squirrel).

M. A. H. SIDDIQI, Lucknow.

The anatomy of the system is described. A detailed account of the neck of the bladder, prostate gland, ductus deferens, and prostatic urethra is given. Special attention has been drawn to the mucous membrane of prostatic urethra which shows two semi-lunar folds, two pairs of culdesacs, and the median verumontanum.

The course and relation of ductus deferens and the ducts of prostate glands has been investigated by means of serial sections of the part. The sections have been traced by a drawing projection apparatus and a magnified reconstruction of the part has been made from which the following observations are recorded :—

The prostate gland is tetra-lobular and situated entirely outside the wall of prostatic urethra.

The prostatic secretion is conveyed by 4 ducts which enter through the muscularis of the prostatic urethra and raise a semi-lunar fold of mucous membrane across the posterior part of urethral cavity and which can be rightly called the ' Genital Fold ' as it conveys the ductus deferens also.

The three pairs of ducts, i.e. ductus deferens and prostate ducts open independently about the same level on the surface of verumontanum near the middle of prostatic urethra.

Prostatic sinus has no ductular opening.



The seminal vesicle and consequential formation of ejaculatory ducts are absent.

Uterus musclicus is absent.

Neck of bladder protrudes into the posterior part of the urethra and forms a semi-lunar fold which may be rightly called the 'vesical fold'.

The paper will be illustrated by lantern slides.

### 35. The course and distribution of the anterior ramus of a typical thoracic nerve in man and certain other mammals.

M. A. H. SIDDIQI and A. N. MULLICK, Lucknow.

Cunningham stated that the nerve lies between the external and the internal inter-costal muscles and this description appears in most of the text-books on human anatomy. Walmsley in 1916 showed that the nerve does not lie between the above two muscles but in a plane deeper to the internal inter-costal.

Stibbe, David, and Gladston in 1932 described four musculo-fascial planes in each inter-costal space and that in each space the main nerve lies with a collateral nerve deep to the internal inter-costal. They deny the existence of any nerve between the external and internal inter-costal muscles.

The investigation is based on the dissection of inter-costal spaces of 60 human thoraxes of different ages and a comparative study of the same on dog, cat, rabbit, monkey, goat, and lamb.

The conclusions arrived at are the following :—

#### (A) Human—

There are five muscles in each inter-costal space, arranged in three planes :—

(a) External inter-costal.

(b) Internal inter-costal.

(c) Sub-costal, intra-costal, and transversus thoracic, connected to each other by the endothoracic fascia.

The main nerve lies between the internal inter-costal and the innermost musculo-fascial plane.

A big collateral nerve is given out in some spaces only and occupies the same plane as the main nerve.

A long branch of the main nerve is present between the external and internal inter-costal muscles and supplies these muscles.

#### (B) Other animals examined—

Arrangement of musculo-fascial planes and the main nerve is in general identical to human being.

Collateral nerve is absent in every case.

A long muscular branch between the external and internal inter-costal muscle is present in every case.

Paper will be illustrated with lantern slides.

### 36. A case of human ischiopagus double monster.

M. A. H. SIDDIQI, Lucknow.

The digestive and genito-urinary system of a human ischiopagus double monster foetus has been described and the points of special interest summarized below have been discussed and explained embryologically.

A common anterior abdominal wall, navel, genital tubercle, and peritoneal cavity are present.

There is a single common colon into which small intestines of both foetuses are continuous.



The anal canal is absent, the distal end of common colon opens by an orifice into a common bladder cavity.

The common urinary bladder presents a transverse ridge, showing its double origin.

There are two urethral canals, tracking towards the common genital tubercle.

The ductus deferens terminates on the bladder wall. Its continuity with the urethral canals is not traceable.

Paper will be illustrated with lantern slides.

### 37. Arrangement of superficial veins of cubital fossa in Indians.

M. A. H. SIDDIQI, Lucknow.

The investigation has been carried on 400 human beings of both sexes. A blood pressure instrument tourniquette was applied to the upper part of arm and the prominent obstructed veins were marked by a skin pencil and later charted out on cyclostyled cubital fossa sketch sheets. Various types of arrangements are classified. A comparison has been made with various arrangements as found in other nationalities and reported by Kiknokamoto (Tokyo) in Japanese, Berry and Newton, in Australian born British, C. M. Charles, in American Negro males and American white males.

Paper will be illustrated by lantern slides.

### 38. The developmental stages of *Palæmon lamarrei* H.M.-Edw.

K. N. DAS, Calcutta.

Very little is known about the life-history and developmental stages of Indian freshwater prawns and shrimps. Early stages from the egg onwards of *Palæmon lamarrei* H.M.-Edw., a common freshwater shrimp of Bengal, were reared in the laboratory. In this paper descriptions are given of a number of stages within the egg case and of free stages till the adult characters of the prawn are developed.

### 39. Structural modifications of the pelvic fins and basipterygia of the torrential fishes, with special reference to the function of adhesion.

DEV D. MUKERJI, Calcutta.

Fishes and other animals that inhabit torrential streams have undergone remarkable structural modifications which can be directly correlated with their life in swift currents. Of the diverse structural peculiarities exhibited by the torrential fauna, there are none so interesting and instructive as those that are associated with attachment and progression on smooth rocks and stones in torrents. Certain torrent-inhabiting fishes have developed vacuum suckers, striated pads of skin on the chest region, broad and papillated or striated lips, etc., for adhesion; but in all cases the paired fins, specially the pelvics, which are extensive and horizontal in position, are the most important agency for attachment.

The present paper deals with a comparative study of the modifications of the pelvic fins, the basipterygia and the associated structures of certain highly specialized torrential fishes of India and other countries. It is shown that *adaptation* to environment is no more than a series of functional adjustments of the organisms to varying external conditions of their existence. Under the stress of the environment structures become modified in a variety of ways to serve new functions and thereby to bring about a close adjustment between the organisms and their changing habitats. It is further indicated that structural modifications of the pelvic fins and their associated structures, like other adaptive structures, are, almost in all cases, of distinct utility to the species concerned.



40. A study of the otoliths of *Psettodes erumei* (Bl. Schn.).

S. RANGA RAO, Madras.

The otoliths of a hundred specimens varying in size from 8.0 cms. to 40.0 cms. were examined with a view to find out how far they are useful as indicators of age.

The zones of growth are seen. The boundary lines between successive zones are distinct and definite in many cases. A complete zone is considered to be the result of a year's growth. The otoliths of most specimens collected during August and September show distinct beginnings of the formation of an opaque ring at the outer edge which seems to be due to better conditions of growth. This opaque ring marks off the previous year's growth.

Observations on the stomach contents and the gonadal condition point out that the period from August to September is more favourable for growth. The breeding season probably commences from about October.

The lengths of the specimens are correlated with the respective lengths of the otoliths and the co-efficient of correlation is found to be 0.95.

An attempt is made to sort out the specimens into age-groups according to the number of zones present on the otoliths. The average growth of the several age-groups is shown.

41. The anatomy of the adhesive apparatus in the tadpoles of *Rana afghana* Günther, with special reference to the adaptive modifications.

J. L. BHADURI, Calcutta.

Ranid tadpoles show a great diversity of form and structure which can be correlated with life in different types of habitats. The tadpoles of *Rana afghana* live in torrential streams and show certain adaptive specialization in their structures enabling them to adhere to rocks and stones in swift currents.

Broadly speaking the process of adhesion in *R. afghana* tadpoles is carried on by two distinct structures: the cement organs and the suckorial disc. The cement organs act as a powerful adhesive structure in the nascent larval stages, while the suckorial disc acts throughout the life of the tadpole. The lips of the tadpole which are provided with several rows of backwardly directed teeth also act as powerful organs of attachment.

A histological description is given of the cement organs and attention has been directed to the 'brush-border' fringing the gland cells of the cement organs.

Anatomy of the muscles of the disc is fully described. The homologies and the functions of the muscles are discussed. A histological account of the skin area of the disc is also appended. An attempt has been made to show a definite correlation between the modified structures of the adhesive organs and the habits and habitats of the tadpoles.

## 42. On a new trematode from kingfisher.

G. S. THAPAR and M. B. LAL, Lucknow.

Several specimens of the form described in the present communication were obtained from the intestine of a kingfisher shot at Lucknow; they belong to the family Psilostomidae and present the following characters:—

Absence of the body spines; Y-shaped excretory bladder; ovary in front of the two testes, situated in the middle of the body behind the ventral sucker; vitellaria not meeting in the middle at the posterior end of the body; relatively long uterus with large number of eggs; dextral



position of the genital pore; vesicula seminalis situated in front of the ventral sucker; cirrus short and plumpy.

These characters are such that they are not present collectively in any of the hitherto described forms of the family, though certain characters are present in different forms.

A detailed account of the anatomy of the worm is given and is followed by a discussion on its systematic position.

#### 43. Burrows of *Thalassema bombayensis*.

P. R. AWATI and D. S. DESHPANDE, Bombay.

The burrows usually have a more or less permanent aspect and may be approached by two entrances. At low water broad areas are left bare, but *Thalassema* drills its home in such a place that the entrance is not uncovered by the lowest tide. The burrowing is performed by the combined action of the proboscis, the swollen anterior region of the body with its ventral setæ and the waves of the muscular contractions which pass along the body from behind forward. The proboscis is protruded, and passed into the sand and withdrawn full of sand and again everted. The body is thrust forward partly by the action of the longitudinal muscles of the body wall, and partly by the peristaltic waves produced by the circular muscle by means of which the anterior end is rendered swollen and tense, and is thus enabled to enlarge the burrow. Also the ventral setæ take part in scraping of the unnecessary corners. By these means a passage is cut through the sand and smoothed by contact with the skin, and may be lined with mucus secreted by the epidermis. After burrowing vertically downwards to a depth of from 1 to 2 feet it makes a horizontal or oblique gallery, and then a second vertical one, which opens on the surface of the sand in a funnel shaped aperture. The burrow is never carried deep, has two entrances and is perpendicular and the bottom horizontal. Even in the institute aquaria these animals prepare their burrows in the form of expanded U which can safely be said to be their natural instinct. The apertures of ventilating doors are small, being about one-third the diameter of the tunnel itself. Around one of the openings there is a considerable amount of castings. The greatest distance between their natural burrows measured 45 inches, the shortest 16 inches. Twenty-six was the average for many measurements. The distance between the two entrances depends upon the size of the animals but this is not always the case, for at times even a small specimen may have more extensive burrows for their size than larger ones. The largest specimen obtained was 20.5 inches long when relaxed in anæsthesia and the smallest one an inch.

#### 44. Food getting in *Thalassema bombayensis*.

P. R. AWATI and D. S. DESHPANDE, Bombay.

The method employed by *Thalassema* to gather nourishment is no doubt unique in nature and furnishes a striking example of the adaptive nature. The ventral cilia of the proboscis and the flask shaped mucus glands of the same play here the most active part. These mucoid glands secrete a thin film over the surface of the water which interposes small organisms, and when this so-called townet is fully loaded, is driven towards the mouth by the currents produced by these ventral cilia. Here the proboscis also plays a good part in prehension of good material and by definitely seizing the prey and rolling into the mouth.

#### 45. Respiratory movements in *Thalassema bombayensis*.

P. R. AWATI and D. S. DESHPANDE, Bombay.

There are two separate movements which would be considered under two headings: (1) the peristaltic movements along the body wall which



pump fresh water along the body into the tunnel, and move that within the respiratory chamber of the body; (2) the inhalations and exhalations through the anus for which there is the muscular chamber resembling that of a Holothurian, which is the power house which supplies the chief motive power.

The peristaltic movements of the body serve to propel fresh water in the burrow. The wave which expands the body to fill the burrow, begins at the anterior end and pass along the body posteriorly. As the wave arises at the posterior end a fresh one begins at the anterior end and this is continued for sometime. Afterwards there is a short pause and now the wave begins from the posterior end. This cycle is repeated off and on. The *Thalassema* is always in control of the water and senses anything which may attempt to pass through the burrow.

The inhalations are from one to upwards of 20 in succession before exhalation takes place. The exhalations are usually a single discharge. The rate of breathing is not uniform. At times four inspirations covering 25 seconds were followed by an expiration period of 10 seconds, while in another instance 10 inspirations occupied 30 seconds the expirations only five; twenty inspirations occupied six seconds, the single expiration forty seconds; thirty inspirations occupied forty-five seconds the expirations only twenty. These timings were taken on a specimen in the laboratory aquaria.

#### 46. On developmental Cranioschisis in the embryo of dog.

D. S. DESHPANDE, Bombay.

Malformations and anomalies affecting mammals and lower animals are not uncommon. The following is an interesting case of cranioschisis on the embryo of dog. The crown rumps length of the embryo is 10 mm. In all respects the embryo was normally developed except for the extensive acrania. The entire roof of the skull is lacking and the brain and its membranes are reduced to small uneven masses of tissue lying upon the floor of the skull. The brain showed a flattened and grooved structure widely open up to the first cervical vertebræ. The masses of the brain tissue appeared raised above the level of the defective skull like a turban unevenly tied.

Normally the neural tube is formed from the neuroderm extending along the dorsum of the embryonic disk. The neuroderm layer gets thickened, a groove appears along the middle line, and the margins are raised above the surface of the embryo, forming the neural groove. The margins of the band grow upward and finally fuse with each other throughout their entire length in the middorsal line. The surface ectoderm then separates from the line of fusion and forms a continuous layer upon the dorsum of the embryo thus leaving the neural tube extending the entire length of the embryo immediately beneath the ectoderm.

The formation of the neural tube is the fundamental process and occurs in the embryo at an early period. It is obvious that any interference with its development will be followed by serious defects in the nervous system and the structures that immediately surround it. A most natural result of such interference would be the failure of two margins of the neural groove to unite and it is not improbable that the form described above is the result of imperfect or complete lack of closure of the cephalic end of the neural groove.

#### 47. A report on a bull-frog (*Rana tigrina*) devouring a sparrow.

D. S. DESHPANDE, Bombay.

While dissecting a full-grown bull-frog (*Rana tigrina*), measuring 6 inches in length and 2.5 inches in breadth, obtained from the College tank,



it was seen that the region of the stomach was very tense and abnormally swollen. On opening I was surprised to find a nearly full-grown sparrow inside its stomach. The sparrow measured 3 inches in length and 1.5 inches in breadth. The bird had undergone partial digestion at many places.

The frog in all other respects was quite normal save for an unusual bulging of the abdominal region. The stomach measuring 2 inches in length and 1.5 inches across the diameter, was very distensible.

It may, at first sight, seem impossible that the frog had attacked the sparrow while it was alive. It is however possible that the sparrow while in search of its prey must have fallen in the water. No doubt, the frogs in the tank must have suffered long starvation and hence all had made a bold step in attacking the prey. The largest and strongest must have been successful in his attempt to swallow the bird though it had to undergo great discomfort.

48. A new species of thrips from S. India (*Tæniothrips cardamomi*, sp. nov.).

T. V. RAMAKRISHNA AYYAR, Coimbatore.

During a recent study of some insects and other pests of the cardamom plant in two or three tracts in South India, a species of 'thrips' was noted causing appreciable damage to the cardamom capsules in an estate on the Anamalai hills in South India. On a special study and comparison of this insect with the allied forms of the group in the Thysanoptera, it was found to be a species not named or recorded so far. It is, therefore, described in this paper, especially because it has some economic importance and agricultural entomologists would like to get the insect properly named for future reference. It is named after its food plant—*Tæniothrips cardamomi*, n.sp.

49. On the morphology of a new trematode of the genus *Haplorchis* from the intestine of *Pseudeutropius taakree*.

J. DAYAL, Lucknow.

A large number of trematodes were collected from the intestine of *Pseudeutropius taakree*.

Only two species *H. cahirinus* and *H. pumilio* of the genus *Haplorchis* (Looss, 1899) have been described. Of these, Witenberg (1930) considers *H. pumilio* to be identical with *Monorchotrema taihokui*.

The present species resembles *H. cahirinus*, and is interesting as it will be a second species of Heterophyidae found in the adult stage in the intestine of a fish (if Witenberg is correct), *H. cahirinus* being the first. The new form presents many differences from *H. cahirinus*, chiefly in the size of the intestinal cæcæ, in the relative size and position of the genital organs and the size and position of the receptaculum seminis. All these differences along with other minor differences indicate that the form is a new species.

The paper concludes with a short discussion on the classification of the sub-family Haplorchinæ (Looss, 1899).

50. A note on a Pangolin, *Manis crassicaudata* found in H.E.H. the Nizam's Dominions.

M. RAHIMULLAH, MOHD. A. R. KHAN, and B. K. DAS,  
Hyderabad (Deccan).

Two species of Indian Pangolins, viz. *M. crassicaudata* and *M. pentadactyla* are known to be distributed in various parts of India; the



former with 11 to 13 longitudinal rows of scales over the body occurs practically throughout the Peninsula, whereas the latter with 15 to 19 rows of scales is limited to Himalayas, Sikkim, Assam, and Burma. The specimen under investigation was approximately a full-grown ♀ *M. crassicaudata* found at an altitude of about 1,450 ft., and measuring 39.5 cms. (including the head=7.5 cms.) in length, and the tail is 30 cms., and the greatest girth of the body is 41.2 cms.

The body is covered with scales (average size: 6 cms.  $\times$  4.9 cms.) arranged in an imbricate manner, the undersurface being quite free, whereas the tail (bluntly pointed) is covered all round with scales. The scales on the head (which are absent on the ventral surface) present a beautiful diamond-shaped appearance and become gradually reduced to a very small size towards the snout. Scales are, however, absent from the preaxial sides of both the fore- and the hind-limbs. Immediately over the region of the thigh-joint, there is a patch of skin which is scaleless, whereas in the case of the fore-limb there is no such gap. Soft bristles are sparsely distributed over the back, the legs, and the tail.

The digits are provided with claws which are very strongly developed on the fore-feet in correlation with the digging habit, and amongst these the 3rd claw being the largest—the one on the fore-foot is nearly 3 times the size of that on the hind-foot.

As regards colouration it is light brown all over, the undersurface being much paler; and the ventral surface of the head being brownish grey, whilst the snout is light grey.

The walls of the stomach have few folds and are fairly smooth in character, whereas the pylorus is nearly twenty times as thick, and its mucous membrane is considerably hardened and rough in appearance.

Numerous nematode parasites have been found in the rectum, which have been studied.

## 51. On the pyloric cæca in the family *Notopteridæ*.

M. RAHIMULLAH, Hyderabad (Deccan).

At the last Science Congress, with a view to make a systematic survey of the pyloric cæca amongst the fishes found in India the author, to start with, had described the condition of the cæca as found in the Family Ophiocephalidæ, and this year he proposes to discuss the structure of the cæca in the family Notopteridæ.

In *Notopterus notopterus*, Pallas, lying immediately below the large gas-bladder is the intestine which is short and simple and is disposed in a semi-circular loop; and below the latter (and almost hidden between it and the globular stomach) are the two cæca, viz., the *dorsal* (larger) and the *ventral* (smaller) cæca, which are very closely situated together and run parallel to the intestine, the pylorus being very small.

In a fish measuring 24.4 cms. in length the ratios of the lengths of the dorsal and the ventral cæca (each taken as a unit) to those of the intestine and the whole of the alimentary tract are nearly 1 : 2.5 and 1 : 4; and 1 : 3 and 1 : 5 respectively. Both the gastric and the intestinal branches of the coeliac artery supply them with oxygenated blood, whilst the venous blood from these structures is drained by the intestinal factor of the Hepatic Portal vein. The left visceral branch of the vagus innervates the stomach as also both the cæca, whereas its right counterpart supplies the stomach, the intestine, and the dorsal cæcum.

Complete histological details of these two cæca have been studied and compared with those of the Ophiocephalidæ. They belong to the simplest type found in *O. gachua*, and present more or less feather-like appearance in section. Curiously enough, the mucosa of both the intestine and the cæca possesses finely ciliated epithelia.



52. Report on some poisonous snakes found in Hyderabad (Deccan).

B. K. DAS, Hyderabad (Deccan).

Four distinct species of poisonous snakes (as also found in certain other parts of India) have come under the notice of the author. The cobra (the 'Gokhura' or 'Nag sâmp'—the spectacled or the biocellate type), *Naia naia* is quite common: the monocellate variety (i.e. the 'Keutiah') seems to be absent. Nearly all the cobras found here are either brown or olive-brown in colour, having a distinct spectacle mark on the hood, and only a few are blackish. Next comes the Russell's viper (the 'Daboia' or 'Chandrabora'), *Vipera russelli*, locally called 'Pinjara' (and its younger forms known as 'Chirgoo' and supposed to be the most venomous snake of this place), which is equally common, and is usually met with amongst low bushes and very often in areas thickly covered over with *Cactus*. Majority of deaths are due to the bite of this viper. The common 'Krait' ('Dhomum Chitti' of N. India), *Bungarus caeruleus* is not so common as the other species, whereas the banded 'Krait' or 'Raj sâmp', *Bungarus fasciatus* is the least common species, having dark cross bands over a light brown background.

Various other details have also been discussed.

53. Partial hermaphroditism in *Rana tigrina*.

SHADI LALL, Lahore.

In an adult functionally male specimen of *Rana tigrina*, caught from a dirty *nala* across Lahore railway lines near Landa Bazar, the author chanced to discover on 22nd May, 1934, during demonstration work certain abnormalities in its reproductive system. The animal gave no definite clue of the sex from outside. On dissection it showed a pair of unequal testes, the right one being about half the size of the left. A pair of complete well-developed oviducts were also present. Both the uteri and the urino-genital ducts were seen to run in close contact opening separately in the cloacal chamber. No trace of the ovary, however, was discovered.

So far two nearly identical cases of hermaphroditism have been recorded in *R. tigrina* in India; one by Bhattacharya and another by Bhaduri. This is a third instance of its kind recorded, for the first time, from the Punjab.

54. A study of two species of *Typhlops* found in Lahore.

HAFEEZ ULLAH, Lahore.

The paper contains an account of two species of *Typhlops* occurring in Lahore, one of which is *T. braminus* and the other appears to be new to science.

Some interesting points with regard to the anatomy, morphology, and habits of the two species are dealt with in the paper.

55. Preliminary observations on the morphology and bionomics of the House-shrew (*Crocidura caerulea*).

K. L. MALHOTRA, Lahore.

The author has been engaged in a study of the House-shrew since June, 1934. Specimens of this species have been collected from Lahore and its suburbs, and other localities in the Punjab, such as Muridke and Haranpur.



According to Dobson *Crocidura caerulea* is a semi-domesticated form of *Crocidura murina*. This view is not corroborated by the author's observations.

Attention is directed in this paper to certain features of interest in regard to the skeleton.

## 56. The development of the male genitalia of the house-fly (*Musca nebulo*).

NASEER-UD-DIN, Lahore.

In the adult house-fly the male genitalia consist of a median copulatory organ. The aedeagus, two pairs of lateral processes, the parameres, and the coxites with their styli and the anal cerci. All of these structures are borne by the 9th or the last abdominal segment.

There is one more pair of accessory forceps situated on the sternite of the 5th abdominal segment.

After the larva has pupated there are found two solid lobes hanging down from the roof of the genital cavity, these are the paramere lobes.

At the next stage of development these paramere lobes divide by a longitudinal fissure into two pairs: an inner and an outer. The two inner lobes fuse along their median lines and form the aedeagus, and the outer pair form the parameres. There arises a pair of appendages from the 9th sternum, each one of the appendages is situated to the exterior of the parameres. These appendages are the coxites. The apical portion of these coxites, during development, are constricted off as their styli.

There arises two appendages from the tergum of the 9th abdominal segment, one on either side of the rectum. These appendages bend down and meet in the mid-ventral line below the rectum. These appendages are the anal cerci. The accessory forceps make their appearance as two hollow outpushings from the posterior side of the sternite of the 5th abdominal segment.

## 57. A preliminary study of the soil Protozoa of Lahore.

AHMAD HUSAIN, Lahore.

92 samples of soil were examined for Protozoa. The following media were used: Hay Infusion, Ashby's Mannite medium, horse dung medium, Shornton's medium, soil as medium and nutrient medium. The paper contains an account of the species found in the samples of soil.

To estimate the presence of Rhizopod tests two methods were tried: (a) Sandon's method of inoculation of soils in tap water and examining at intervals; (b) Winogradsky's centrifuging method. The testaceous rhizopods are commonly met with in peaty soil or acid soil and are hence scarcely found in the Punjab where the soil is usually alkaline.

## 58. Role of the Golgi apparatus in the formation of the acrosome in the male germ cells of the Lahore centipede *Rhysida longipes*.

G. R. GADHOKE, Lahore.

Broadly speaking, there are two views regarding acrosome formation. According to one, the acrosome is a secretory product of the Golgi apparatus; while, according to the other, the Golgi apparatus is directly transformed into the acrosome. In the present paper the author has made an attempt to ascertain which of these two views is correct.

The Golgi bodies form a Golgi apparatus in the young spermatocyte. The apparatus consists of chromophilic batonets, clumped together and enclosing a nonstaining sphere substance. This breaks up into individual Golgi bodies, each composed of a chromophilic crescent enclosing a portion of the sphere substance.



After meiosis, the spermatid is formed. The Golgi bodies aggregate posterior to the nucleus, and later fuse together forming the acroblast, which is composed of a chromophilic outer shell enclosing a non-staining substance within. The acroblast travels to the anterior end of the nucleus and a perferatorium is formed within the non-staining region. The whole structure now is the acrosome.

The acrosome in the Lahore centipede is formed by a fusion of the Golgi bodies, as in the crab *Paratelphusa* (Nath, V., 1932).

The Golgi material is not sloughed off after secreting the acrosome as advocated by Bowen, Payne, and Pollister.

59. The musculature and nerve supply of the genitalia of the *ak*-grasshopper (*Pæcilocerus pictus*) and the desert locust (*Schistocerca gregaria*).

S. S. KAPUR, Lahore.

Specimens were preserved in 5% formalin for the study of the neuromusculature of the genitalia. The arrangement and number of muscles were found to be identical in both *Pæcilocerus pictus* and *Schistocerca gregaria*.

This paper contains an account of the boring habits and the part played by certain genital sclerites in egg-laying as well as the action of certain muscles of the genital segments in respiration.

Nerve supply to the genital muscles has also been investigated.

60. Some entomostraca from Karachi.

G. L. ARORA, Lahore.

The author made a collection of marine Entomostraca from Karachi both inside and outside the harbour in December, 1933, and January, 1934. The list of Entomostraca given in the present paper is yet incomplete. The order Copepoda is represented by nine genera, viz., *Calanus*, *Eucalanus*, *Paracalanus*, *Acrocalanus*, *Candacia*, *Temora*, *Centropages*, *Pontella* and *Acartia* while the genus *Evadne* is the only representative of the Cladocera.

A statistical statement of these genera is also given in the paper.

61. Incidence of Helminthic parasites in cattle in Lahore.

SUKH DYAL, Lahore.

During October, 1933, and April to May, 1934, the author used to visit the Beef Slaughter House, Lahore, in order to determine the incidence of Helminthic parasites in cattle. In the course of 40 days he examined 1,043 animals, of which 1% were infected with *Fasciola*, 2% with Cestodes, 14% with Paramphistomi, 20% with Bladder worms, and 8% with *Filaria*, i.e. in all 458 animals or 45% were infected. *Filaria* (all *Bos indicus*) seems to be harmless to its hosts.



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# INDIAN SCIENCE CONGRESS.

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Twenty-second Annual Meeting,  
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ABSTRACTS OF PAPERS.

Section of Chemistry.

*President :—Dr. A. C. Sircar, M.A., Ph.D., P.R.S.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Chemistry.

### *Abstracts.*

1. Magnetic susceptibility of some cobaltic salts and their constitution.

P. R. RÂY, Calcutta.

Determination of the magnetic susceptibility of cobaltic sulphate, cobaltic alum, cobaltic cyanide, and cobaltic carbonate indicates a magnetic moment of two Bohr's magneton for the cobaltic ion. This cannot be accounted for on the basis of the accepted view regarding the magnetic moment of the ions of the first transitional series. An explanation has been suggested in conformity with the constitution of the salts.

2. Micro-determination of zinc in presence of the metals of the iron group by means of quinaldinic acid.

P. R. RÂY and M. K. BOSE, Calcutta.

Zinc has been determined micro-chemically as zinc quinaldinate with quite good results in the presence of iron and aluminium, using alkaline tartrate solution to prevent precipitation of the latter.

3. On the structure of  $\text{CO}_3$  and  $\text{NO}_3$  ions.

P. B. SARKAR, H. C. GOSWAMI, and B. C. RAY, Calcutta.

The ordinary accepted octet theory of valency assumes that in carbonate and nitrate ions one of the oxygen atoms is connected by a double bond whereas the remaining two are connected each by a single bond to the C and N atom respectively. A critical study of the various data obtained from physical measurements, namely the X-ray, infra-red, and Raman-spectra conclusively prove that all the three oxygen atoms are equivalent, the carbon and the nitrogen atoms forming, in respective cases, stable sextets. Thus the structure of these ions can be represented by any of the three following schemes: (1) A flattened pyramid with an equilateral triangular base; the carbon or nitrogen atoms are at the top and the oxygen atoms at the three apices of the base; (2) A plane equilateral triangle with carbon or nitrogen at the centre and the oxygen atoms at the apices of the triangle; and (3) A regular octahedral model. The last model of representation claims molecular dissymmetry and attempts were made to resolve the ion with optically active ( $\text{CoEn}_3$ ) base with negative results. Meanwhile Duval in a preliminary note (*Bull. Soc. Chem.*, T 51, p. 342, 1932) claimed to have resolved the carbonate ion. A careful study of his method and data will reveal that the claim is unjustifiable. We have proved that such resolution cannot be effected.

Of the other two possible symmetrical structures the balance of evidence is, however, in favour of the pyramidal configuration.

4. Triple nitrites of the rare earths: Micro-test for Cæsium.

P. B. SARKAR and H. C. GOSWAMI, Calcutta.

Ball and Abram (*J.C.S.*, 1913, 103, 2110) prepared a number of complex Bismuthinitrites of the type  $\text{X}_3\text{Bi}(\text{NO}_2)_6$  and  $\text{X}_2\text{Y Bi}(\text{NO}_2)_6$  where X stands for  $\text{NH}_4$ , K, Rb, Cs, Tl, and Y stands for Li, Na, or Ag.



The classical work of Prof. Urbain regarding the use of Bismuth salt in the separation and isolation of Rare Earths based on the isomorphic relationship is well known. This led the authors to study whether Cerium forms triple nitrites like Bismuth. The literature gives no description of triple nitrites of the above types.

We have been able to isolate the triple nitrite  $\text{Cs}_2\text{Na Ce}(\text{NO}_2)_6$  in golden yellow octa-hedral crystals by the addition of  $\text{CsNO}_3$  to a mixture of the solutions of  $\text{Ce}(\text{NO}_3)_3$  and  $\text{NaNO}_3$ . The other rare earths, namely La, Sm, Gd, likewise form octa-hedral crystals of the triple nitrites.

Micro-detection of Cæsium as the triple nitrite :—When to a drop of a solution of  $\text{NaNO}_2$  and  $\text{Ce}(\text{NO}_3)_3$  {  $\text{NaNO}_2$  6 gm.  $\text{Ce}(\text{NO}_3)_3$  3 gm. per 100 c.c. of water } a drop of solution containing Cs up to the order of  $0.5 \times 10^{-6}$  gm. is added beautiful yellow octa-hedral crystals are obtained.

### 5. The action of hydrogen sulphide on chromates. Part III— Potassium dichromate.

G. S. KOTWANI, ABDUL HAMID, and H. B. DUNNICLIFF,  
Lahore.

The reduction of 5% potassium dichromate by hydrogen sulphide is attended with rise of temperature which depends on the rate of passage of the gas. The reaction mixture changes in colour from orange through brown, dirty-brown to green.

The brown intermediate solid contains chromium dioxide ( $\text{CrO}_2$ ) and hydroxide, a co-ordinated chromium thiosulphate, chromium tetrathionate and free sulphur. The filtrate contains unattacked potassium chromate, potassium thiosulphate and tetrathionate but no sulphide.

On gradual addition of more hydrogen sulphide the tetrathionate decreases with the amount of chromate until both disappear simultaneously.

So long as chromate is present the test for a sulphide is not given and the dichromate accounted for as thiosulphate is less than theory by the amount of tetrathionate formed.

Thiosulphate is the precursor of the tetrathionate, formed in a side-reaction owing to the mild oxidation of part of the thiosulphate by the chromate. The tetrathionate is ultimately reduced to thiosulphate by the alkaline sulphide, which develops in the reaction mixture as soon as chromate has disappeared.

The final products are—

- (a) a precipitate containing chromium hydroxide, sulphur and a complex chromium thiosulphate in which the ratio of ionic to co-ordinated thiosulphate is 2 : 1, and
- (b) potassium thiosulphate and poly-sulphide in solution.

The polysulphide formed depends on the temperature of the reaction, being  $\text{K}_2\text{S}_3$  at laboratory temperatures and the pentasulphide at temperatures approaching  $90^\circ\text{C}$ .

In the light of previous work on the action of hydrogen sulphide on chromates, it appears that sulphate is not formed in these reductions if the concentration of hydroxyl ions is above a certain critical value and this requires further investigation.

### 6. The action of hydrogen sulphide on chromates. Part IV. —Ammonium bichromate.

G. S. SODHI, ABDUL HAMID, and H. B. DUNNICLIFF,  
Lahore.

The precipitate contains mainly chromium hydroxide, sulphur, thiosulphate also sulphide as well as co-ordinated ammonia and am-



monium ions. Tetrathionate formed by the oxidation of the sulphate by chromate is an intermediate product but the final solution contains only ammonium thiosulphate and (poly) sulphide.

7. The action of hydrogen sulphide on chromates. Part V—  
Ammonium chromate.

G. S. SODHI, ABDUL HAMID, and H. B. DUNNICLIFF.  
Lahore.

The results are similar to those described in part IV, tetrathionate appearing as an intermediate product in this reaction also.

8. The action of hydrogen sulphide on chromates. Part VII  
—Insoluble chromates.

H. B. DUNNICLIFF and BRAHM PRAKASH. Lahore.

At about 10°C., the final product of the reduction of lead chromate contained co-ordinated chromium sulphate, chromium thiosulphate (probably co-ordinated), chromium hydroxide, free sulphur, lead sulphide, and a little unattacked lead chromate.

At about 50 and 70°C., the final precipitates contained the same products, the sulphate and thiosulphate completely account for the oxidising power of the chromate and the free sulphur present is attributable to the oxidation of hydrogen sulphide by oxygen dissolved in water and taken up from the surrounding air and, to a minor degree, by photo-chemical action. Free sulphur in the 'slow reaction' at the lower temperature appears quantitatively as sulphate in the reaction accelerated by higher temperature.

The final precipitate in the reaction with silver chromate contained silver sulphide, chromium hydroxide, co-ordinated chromium sulphate, chromium thiosulphate (probably co-ordinated), free sulphur and chromium sulphite was observed for the first time. This indicates that sulphite is probably an intermediate compound in the development of thiosulphate as suggested in previous papers. Its appearance seems to depend on conditions in which its oxidation to a sulphate or the formation from it of thiosulphate is retarded or rendered impossible by the conditions of the reaction.

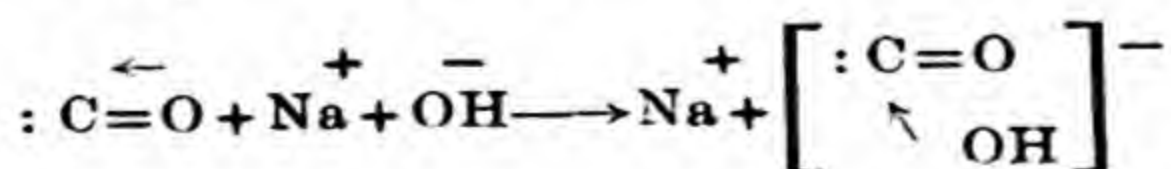
Sulphite was detected once or twice in the reduction of mercuric chromate but was not a constant product of the reaction.

The chromates of magnesium, barium, and strontium give sulphate as well as thiosulphate in the precipitate although the filtrate is very alkaline. Work is proceeding to determine the conditions which limit the formation or non-formation of sulphate in these reactions.

9. Constitution of formic acid and formates.

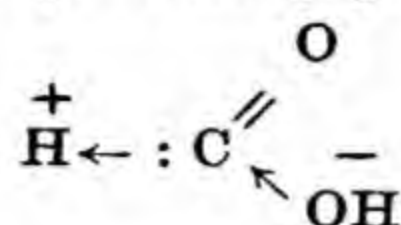
P. B. SARKAR and B. C. RAY, Calcutta.

That formic acid differs from its higher homologues in chemical properties and absorption spectra is an established fact. The acid character of its nitrile, non-existence of acid chlorides and anhydrides, the reducing character of the formate ions, led Richter to exclude it from the homologous fatty acids. These discrepancies are to be sought for in the constitution of the acid itself. Thus in the case of the formic acid the ionizable hydrogen atom is not that of the hydroxyl group, as in the case of its homologues, but the hydrogen atom attached to the carbon itself. The classical synthesis of formates from CO and KOH is explained thus :—





In the formate ion, therefore, the OH ion co-ordinates with the CO group and forms a negative ion in which carbon is practically bivalent and retains a lone-pair of electrons. To this lone-pair the reducing character of formate ion is due. It has been proved in this paper that it is the formate ion which is reducing and neither the undissociated formic acid nor its esters which have practically got a normal structure, namely

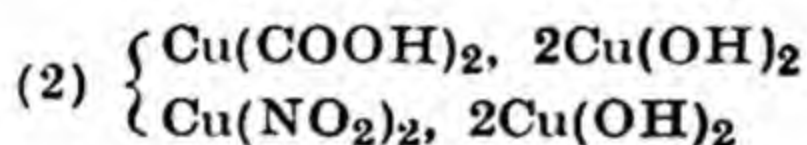
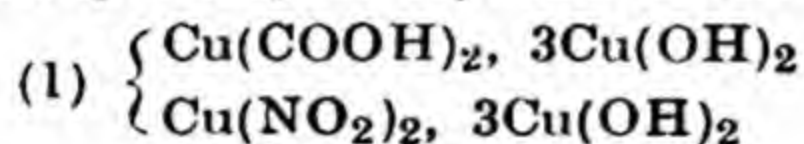


The Raman spectra of the solid  $\text{Cd}(\text{CHO}_2)_2$  has shown no frequency corresponding to the C-H bond exactly what our theory demands.

Comparing the structure of the formate and nitrite ions side by side it appears that, as they are iso-steric and iso-electric, they should exhibit isomorphous relations.

In course of our investigation we have prepared the following mixed crystals :—

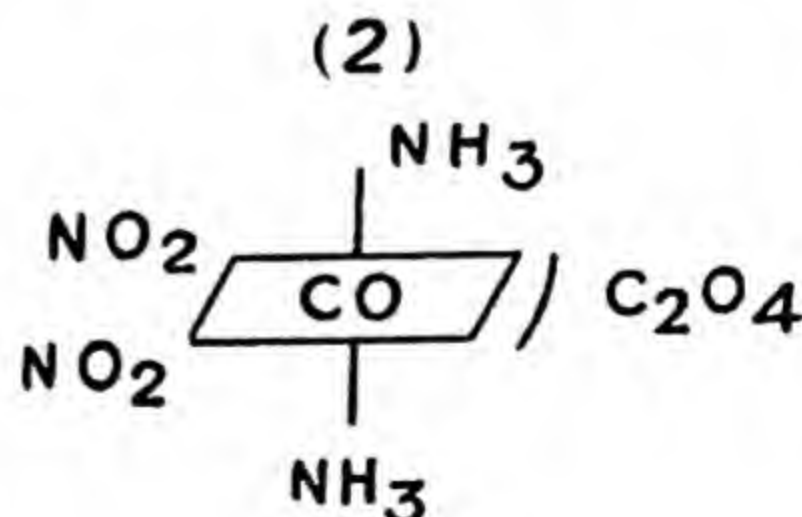
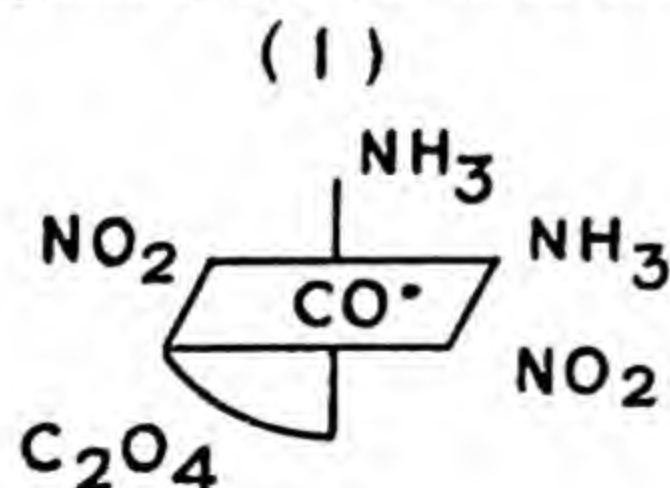
1. Barium (formate, nitrite), barium (nitrite, formate),  $\text{H}_2\text{O}$ .
2. Strontium formate with strontium nitrite.
3. Zinc formate with zinc nitrite although the latter cannot be isolated in the free state.
4. Cadmium formate with cadmium nitrite (miscibility small).
5.  $\text{Mg}(\text{COOH})_2$ , 2 hexamethylene tetramine,  $10\text{H}_2\text{O}$ .
6.  $\text{Mn}(\text{COOH})_2$ , 2 hexamethylene tetramine,  $10\text{H}_2\text{O}$  perfectly isomorphous with the corresponding nitrites.
7.  $\text{KCd}(\text{CHO}_2)_3$  isomorphous with  $\text{KCd}(\text{NO}_2)_3$ .
8. X-ray study of crystals of the following type is in progress :—



#### 10. Constitution of Erdmann salt.

P. B. SARKAR and B. C. RAY, Calcutta.

Contradictory statements, regarding the constitution of oxalato-dinitro-diammine cobaltiate, have been put forward by Shibata (*Journ. Coll. Scien. Tokio*, Vol. XLI, Art 2, 1917) and Riesenfeld (*Zeit. Anorg. Chem.*, 124, pp. 1-24, 1922). Thomas undertook the problem and obtained two sets of crystals by fractional crystallization of the Barium salt (*J.C.S.*, 123, 617-619, 1923). The rhombic variety is said to be resolvable and hence has a cis-cis constitution. The other monoclinic variety is arbitrarily given a cis ammonia-trans nitro configuration (formula 1). In the present paper the writers have studied the constitution of the monoclinic variety from its absorption spectra and chemical behaviour and have proved that it is a trans ammonia cis nitro compound (formula 2) thus supporting the views of Riesenfeld.





## 11. Intermediate compounds formed in the decomposition of chromates.

V. T. ATHAVALE, Bangalore.

A study of the decomposition of mixtures of chromates and oxides of alkaline earth shows only two stages in the decomposition corresponding to 33.3 and 40 per cent., the intermediate compounds formed being (1)  $9(\text{RO}) \cdot 4(\text{CrO}_3) \cdot \text{Cr}_2\text{O}_3$  and (2)  $17(\text{RO}) \cdot 6(\text{CrO}) \cdot 2(\text{Cr}_2\text{O}_3)$ . This disposes off the claim for the formation of the large number of intermediate compounds found in the previous work.

Structural formulæ for these intermediate compounds based on the Werner's conception of valency have been given.

## 12. Hydrogen ion concentration of lead salts.

D. N. MEHTA, Bangalore.

pH values of lead oxide solutions have been determined by quinhydrone, antimony and bismuth electrodes. The results have been compared with those calculated from solubility data and it is suggested that the use of antimony electrode is not suitable in the measurements of pH values of lead salts, whereas the use of bismuth electrode is preferable to the use of antimony electrode because of the less acidic character of the former.

The pH value of solution of  $\text{Sb}_2\text{O}_3$  has been determined, quinhydrone and antimony being employed as indicator electrodes. The value obtained with antimony electrode comes out identical with the value calculated from the solubility data.

The pH values of lead acetate, and specially prepared basic lead acetate have also been determined, bismuth, antimony, and quinhydrone electrodes being employed. Quinhydrone electrode was found the most suitable for the measurement and bismuth found to be better than the former two.

The necessity of pH control in the process of manufacture of white lead (owing to the lack of suitable indicators) has been pointed out as a very convenient means of limiting the nature of the final products.

The measurements of pH values of distilled water, conductivity water have also been carried out using the above electrodes.

## 13. The structure of nitrobenzylalkylamines.

BALWANT SINGH, ANAND SARUP, and H. B. DUNNICLIFF,  
Lahore.

The parachors of ortho-, meta-, and para-nitrobenzyl dimethylamines, nitrobenzyl dipropylamines, and nitrobenzyl dibutylamines have been determined. The values obtained indicated that the ortho-compounds are not chelated and there is no intramolecular co-ordination in these compounds.

## 14. Kinetics of the reaction between $\alpha$ -bromopropionate and silver ions.

A. N. KAPPANNA, Nagpur.

A detailed study of the kinetics of the reaction has been made. Silver bromide formed during the course of the reaction exerts a catalytic effect. The influence of the amount of the catalyst on the velocity coefficient at constant as well as varying ionic strength has been investigated.



15. Kinetics of the decomposition of trichloroacetic acid—  
Part III.

A. N. KAPPANNA and H. W. PATWARDHAN, Nagpur.

The rates of decomposition of the acid under varying conditions of acidity have been determined. An explanation of the mechanism of the reaction has been attempted.

16. Electrolytic reduction of carbonic and formic acids.

V. BHEEMIAH and M. QURESHI, Hyderabad.

The main object of this investigation is (a) to determine the nature of the electrolytic reduction of carbonic and formic acids under varying conditions of electrolysis and (b) to find out the relationship of these reductions with the over-voltage at which hydrogen is evolved at the cathode. This investigation has so far yielded the following results :—

It has been found, in conformity with the conclusions of Coehn and Jahn, that a bicarbonate is fairly rapidly reduced to formic acid on an amalgamated zinc cathode. An aqueous solution of carbonic acid is also reduced to formic acid but the yield is very small.

No formaldehyde is detected even after a prolonged electrolysis extending over 24 hours.

Formic acid alone or in the presence of sulphuric acid is reduced to formaldehyde but when the solution is alkaline no formaldehyde is formed.

The yield of formaldehyde in acidic solutions is small but it increases with the current density and the hydrogen over-voltage. Beyond a particular current density it decreases instead of increasing.

The hydrogen over-voltage in formic acid solutions does not indicate any definite change with the change in the concentration of the electrolyte. It decreases with the rise of temperature. The temperature coefficient is found to be  $-2.8$  millivolts per degree.

The surface of the cathode and consequently the hydrogen over-voltage suffer changes during the course of each electrolysis. There is a tendency for the over-voltage to indicate a small rise in the beginning, but as the electrolysis progresses a gradual fall makes itself evident.

The above results have been critically examined but full discussion is reserved until more experimental facts are available.

17 Anomalous diamagnetism of selenium.

MATA PRASAD and S. S. DHARMATTI, Bombay.

The diamagnetic susceptibilities of the samples of selenium, powdered to different degrees of fineness, have been measured with a magnetic balance of the Wilson type. The diamagnetism of the samples decreases as the fineness of the powder is increased and at a certain stage the sample becomes paramagnetic. The paramagnetic value increases on further powdering. The value for selenium sol has also been measured and is found to be  $0.7001 \times 10^{-6}$  cgs. which is more paramagnetic than any of the powdered samples.

To see if any oxide effect is present we removed the oxide by washing with absolute alcohol and retested the samples; paramagnetism still persists.

18. Studies in gelation, Part I.

M. U. PARMAR, S. M. MEHTA, and MATA PRASAD,  
Bombay.

Methods of Fleming, Fells, and Firth and of Hurd which depend on the change of viscosity of a gel-forming mixture as well as those which



depend on the optical properties of such mixtures have been compared with a view to find out a reliable method for measuring the time of set of silic acid gel-forming mixtures. The results lead to the conclusion that it is necessary to give a definition of what is to be understood by 'time of set of a gel-forming mixture' before any method can be selected for the purpose.

Conductometric titrations of silicic acid gel-forming mixtures have also been made in presence of hydrochloric, acetic, and citric acids.

The results of experiments on the surface tension of both acidic and alkaline gel-forming mixtures show that it decreases slightly at first and then slowly increases reaching a maximum when the gel has set.

### 19. Studies in gelation, Part II.

M. U. PARMAR, S. M. MEHTA, and MATA PRASAD, Bombay.

Various conditions under which thorium phosphate can be obtained in the form of a gel have been studied. It is found that completely transparent, translucent or opaque gels can be obtained by adjusting conditions of their preparation and that they can be prepared only within a limited range of pH.

The time of set of these gels and the effect of electrolytes and non-electrolytes on it have been investigated. In general the electrolytes lower the time of set whereas non-electrolytes increase it.

The effect of temperature on the time of set as well as the formation of Liesegang rings have also been investigated.

Kinetics of gelation in the case of gels obtained by using alkaline phosphate solutions have been studied by an optical method. The time required for a change from a translucent to a transparent gel has been also measured.

These results appear to throw considerable light on the structure of gels.

Various other physical properties such as viscosity, vapour pressure, etc., are being investigated.

### 20. Solutions of sodium zincate.

S. M. MEHTA and M. B. KABADI, Bombay.

Pure crystalline zinc hydroxide, prepared according to the method of Dietrich and Johnston (*J. Amer. Chem. Soc.*, 49, 1419, 1927) was dissolved in sodium hydroxide to give solutions containing  $\text{ZnO} : \text{Na}_2\text{O}$  in varying proportions. The concentrations varied from 9N to 0.5N. The electrical conductivities of these solutions have been measured and the results show that the conductivity of sodium hydroxide is diminished by the addition of zinc hydroxide between the ratios 1 : 1.76 and 1 : 3 for solutions not less dilute than 4N. This may be due to the formation of a zincate in these solutions. This seems corroborated by the fact that colourless needle-shaped crystals have been obtained from the most concentrated solutions which on analysis appear to be those of a definite zincate. It is also observed that a crystalline precipitate which is probably zinc hydroxide separates from solutions less dilute than 4.5N on standing for some time. Further work is being continued on an examination of various properties of these solutions and those of the crystals.

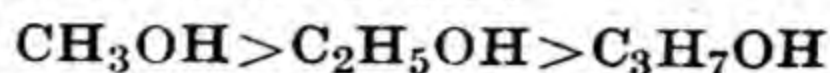
### 21. Studies on titanium dioxide sol.

S. M. MEHTA and MISS OLIVE JOSEPH, Bombay.

The changes in the viscosity of the titanium dioxide sol dialysed and diluted to different extent have been measured in presence of mono-, di- and trivalent electrolytes, using Scarpa's method with suitable modifications. The viscosity at first increases, reaches a maximum, and then



begins to decrease. The time-viscosity curves are not 'S' shaped as observed by Gann. If, on the other hand, these measurements are made in the presence of mixtures of electrolytes and alcohols the viscosity rises to a maximum as in the case of electrolytes alone but the time-viscosity curves are 'S' shaped. It is found that the alcohols exert a peptising influence on the coagulation of the titanium dioxide sol. The peptising influence of the alcohols is in the order :



Changes in the pH of these sols have also been measured.

## 22. Electrical conductivity of solutions of sodium phosphate.

S. M. MEHTA and S. M. SHETH, Bombay.

The electrical conductivity of solutions containing sodium hydroxide and orthophosphoric acid in varying proportions expressed in terms of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  in the ratios (i) 1.5 : 1, (ii) 1 : 1, (iii) 1 : 1.5, (iv) 1 : 2, (v) 1 : 2.5, (vi) 1 : 3 have been measured at various dilutions between 2N and 0.005N at 30°C. It is found from the equivalent conductivity-ratio curves that the electrical conductivity of these solutions decreases at first as the ratio is changed from 1.5 : 1 to 1 : 1 and then begins to increase. The minima obtained in the curves appear to correspond to  $\text{NaH}_2\text{PO}_4$ , i.e. to the neutralisation of the first hydrogen of phosphoric acid. It is also observed that the minima are more marked in dilute solutions than in concentrated ones. The observed increase in conductivity with an increase in dilution is expected as being due to increased dissociation of the salt in solution.

The pH of these solutions are being measured by the electrometric method.

## 23. Reaction between solutions of sodium phosphate and mercuric chloride.

S. M. MEHTA and S. M. SHETH, Bombay.

Mellor (*Treatise on Inorganic Chemistry*, Vol. V, p. 17) states that a solution of mercuric chloride reacts with one of borax giving a red precipitate and that this reaction is sometimes styled G. Tammann's reaction for free borates. It is found that a similar precipitate can be obtained by the interaction of a solution of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  with that of mercuric chloride : the colour and composition of this precipitate can be varied by adjusting conditions of precipitation. A search of literature has revealed that similar precipitates have been obtained by Haack (*Liebig. Ann.*, 262, 188, 1891) but that he has investigated the problem from a different standpoint. The variations in the colour and composition of the precipitates obtained by the reaction between solutions of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and of mercuric chloride as well as the change in the specific gravity and other properties of the precipitates have been investigated under different conditions. The results show that the physical properties of the precipitates are correlated with the pH of the alkali phosphate solutions.

## 24. An X-ray investigation of the crystals of Benzoin.

MATA PRASAD and JAGDISH SHANKAR, Bombay.

Benzoin was prepared by shaking together pure benzaldehyde and pure potassium cyanide in a sealed glass tube at 100°C. The crude product was purified by repeated crystallizations from rectified spirit. Well-developed crystals were obtained by the slow evaporation of the solution of the substance in alcohol.



The crystals were investigated by the Rotation Method using a Shearer gas tube and a copper anticathode. The dimensions of the unit cell were found to be

$$a=19.7\text{\AA}, \quad b=5.81\text{\AA}, \quad c=10.5\text{\AA}, \quad \text{and} \quad \beta=106^{\circ} 52'.$$

Oscillation photographs were taken at intervals of  $15^{\circ}$  about the  $b$  and the  $c$  axes and a large number of planes were identified. It was found that the (hol) planes are halved when  $h$  is odd. This halving corresponds to the space group  $C_{52h}^5$  with  $\overline{1}m$  Bravais lattice. The number of molecules required by the space group is 4 and that calculated from the dimensions of the unit cell and the density of the crystal is also 4. The molecules in the cell are therefore asymmetric.

Further work on the measurement of the intensity of reflection from various planes will shortly be undertaken in order to elucidate the orientation of the molecules in the cell.

## 25. Pharmaceutical emulsions.

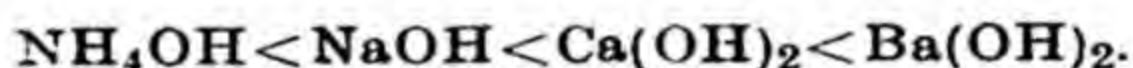
N. P. CHATTERJEE, Calcutta.

Several pharmaceutical emulsions were found, on test, to contain 30 to 40 per cent. oil, about 1 to 20 per cent. emulsifier and the pH values of the emulsions were between 4.5 to 5.5. The size of the particles was of the order of 1.5 to  $80\mu$ . The paper deals with the experiments and discussions on the preparation of emulsions with such properties. The advantages of using combinations of emulsifiers have been pointed out.

## 26. Titration of colloidal acids.

J. N. MUKHERJEE and S. MUKHERJEE, Calcutta.

Electrometric titrations of colloidal solutions of Palmitic acid have been carried out against different alkalies. The total acidities calculated from the titration curves are found to vary with the alkali employed in the order



The results have been discussed with reference to the constitution of the double layer surrounding the particles.

## 27. On the measurement of the absolute rates of migration of ions by the method of moving boundaries.

J. N. MUKHERJEE, R. P. MITRA, and A. K. BHATTACHARYYA, Calcutta.

The method of moving boundaries has not hitherto been applied for a direct determination of the absolute rate of migration of an ion from an actual measurement of the potential gradient at the boundary. An attempt in this direction has been made following Mukherjee's method of measuring the cataphoretic speeds of colloidal particles. The observed potential differences between two fixed planes at right angles to the direction of the current, when a hydrochloric acid-picric acid boundary moves between them, have been found to vary regularly (i) with the distance swept by the boundary and (ii) with time. These variations have been utilized for calculating the absolute rates of migration of the chloride and the picrate ions. Better reproducibility is obtained with the more concentrated solutions where variations from mean values are within 1.5 per cent. The results appear to depend upon factors operating at the boundary in a manner not contemplated in the simple Kohlrausch theory.



## 28. On the nature of colloidal acid clay.

J. N. MUKHERJEE and R. P. MITTRA, Calcutta.

Acid colloidal clay has been separated from different samples of soil with the help of the Sharple's supercentrifuge. Simultaneous potentiometric and conductometric titrations of these acid clays have been carried out using different alkalis. The titration curves for a given specimen show (i) that the buffer action towards given additions of alkali depends on the nature of the alkali itself and (ii) that the time of interaction is also an important factor. Titration with acids have been carried out in order to ascertain to what extent these acids act as amphoteric electrolytes and react with hydrogen ion to form aluminium ions.

## 29. On the nature of colloidal acids.

J. N. MUKHERJEE, S. C. GANGULY, and B. CHATTERJEE, Calcutta.

In continuation of our previous work on colloidal acids, improvements in technique have been introduced. They include: (1) stocking the sol in an atmosphere of hydrogen free from all contaminations; (2) precautions for preventing leakage from mains, etc.; (3) efficient arrangement for shaking the system during titrations.

As a result of these improvements silicic acid sols could be preserved unchanged for months, and reproducible electrometric measurements could be obtained even at high dilutions.

The electrometric titrations of silicic acid sols against alkalies generally confirm our previous observations on the nature of colloidal acids. Buffer action is observed during titration in high pH regions.

## 30. Purification of activated charcoal with reference to its electrical charge and its variation with concentration of electrolytes.

S. P. RAYCHAUDHURI, S. K. NANDI, and J. K. BANERJEE, Calcutta.

Various samples of sugar charcoal have been washed and boiled with conductivity water for a long time and at different stages of washing the conductivity of the supernatant liquid and the electrical charge of the resulting sample have been measured.

All samples of charcoal which initially possessed a negative charge attained a zero charge and in two cases ultimately became positive. This confirms previous observations from this laboratory.

Variations of the electrical charge of negative and null charcoals in contact with solutions of acids, bases, and salts have been measured.

Various theories of adsorption of electrolytes by activated charcoal have been discussed in the light of the experimental results.

## 31. On a new type of liquid junction.

D. N. GHOSH and P. B. GANGULY, Patna.

The presence of liquid junction potentials is a source of considerable difficulty in the accurate measurement of E.M.F. of cells as owing to their instability their values cannot be accurately determined. Previous attempts have been directed towards decreasing the interfacial area of the contact and towards lowering the concentration gradient of the junction solutions. A type of liquid junction has been developed where in addition to decreasing the interfacial area diminished diffusion has been secured by decreasing the time of contact of the solutions at the junction.



Series of determinations have shown that this type of junction gives constant and reproducible values. Experiments with junctions of the free diffusion type and the continuous mixture type used by Guggenheim have also been conducted for comparison.

### 32. Studies on the vapour pressures of emulsions.

P. B. GANGULY, Patna.

The vapour pressures of a series of oil-in-water and water-in-oil emulsions have been measured. A type of apparatus suitable for the above measurements is described. It has been found that the vapour pressures of the emulsions generally approximate the values for the liquid forming the continuous phase. Advantage might be taken of this behaviour to definitely fix the type of an emulsion.

### 33. Viscosity of dilute solutions of non-electrolytes.

BALBHADRA PRASAD, Cuttack.

The study of the viscosity of dilute solutions of non-electrolytes about which a note was published in the Chemistry Section of the Science Congress last year, has been further pursued. The formula derived connecting viscosity and concentration is  $\frac{\eta}{\eta_0} = 1 + \alpha c$  when  $\eta$  and  $\eta_0$  are the viscosities of the solutions and the pure solvent respectively,  $\alpha$  is a constant which should be independent of temperature and solute. While it is found that  $\alpha$  is independent of temperature in the cases of cane sugar, fruit sugar, and grape sugar solutions it is not independent of the solute used. How it varies with the solute is being investigated.

### 34. Viscosity and molecular association.

BALBHADRA PRASAD, Cuttack.

A new method for studying molecular association has been suggested. It has been shown that if a graph be plotted with  $1/T$  as x-axis and  $\log \eta$  where  $\eta$  represents viscosity, as y-axis, then the slope of the curve will be proportional to the molecular weight of the liquid.

The relative molecular association at any two temperatures will be proportional to the slopes at the two temperatures and so relative molecular association can be easily found. It has been shown that the slope which is constant in the case of unassociated liquids is 0.7 times the critical temperatures of liquids on the absolute scale. As no liquid remains associated at about critical temperature the value of the slope determined from the critical temperature even in the case of associated liquids will correspond to the unassociated state. Hence dividing the slope of  $\log \eta$  against  $1/T$  at any temperature by  $0.7T_c$  will give the absolute value of molecular association.

### 35. On the influence of a few organic solvents on the swelling of and the absorption of dye-stuffs by silk fibres.

A. NAGARAJA RAO, Bangalore.

It is a matter of common practice during dyeing to increase its effectiveness by the addition to the dye-bath of several substances either of the nature of electrolytes or non-electrolytes. Among the several factors that are responsible for this increased efficiency, the alteration in the condition of the fibre brought about by a change in the swelling is one of the most important and a detailed and a systematic investigation of this has been undertaken with special reference to silk fibres. This enables us to determine the relationship between the nature of the added substance and the direction of the change.



In this paper the longitudinal and the transverse changes undergone by individual fibres of definite dimensions have been measured under varying concentrations of pyridine, formamide, and the different alcohols enabling us thereby to determine the total percentage increase in volume on swelling. The influence of these substances on the absorption of several direct dye-stuffs by silk fibres has also been quantitatively estimated. The surface properties of the added substance appear to be entirely responsible in effecting any alteration in the extent of absorption although specific influences also are not unlikely.

36. On the solubilities of substances.

A. NAGARAJA RAO and D. V. VENKATASUBBIAH, Bangalore.

Carnelly's thermodynamic relation correlating the melting points and the heats of fusion of solid substances gives us only the natural solubilities which are mostly different from the true experimental values. The divergences have been adduced as being due to the varying shapes of the vapour pressure-concentration curves. It is felt that this relation requires a modification by the introduction of certain specific constants of the solvent of the nature of the dielectric constant and viscosity so as to yield solubility values applicable to specific solutes and solvents.

An explanation for the alternating effect observed with the solubility of some of the homologous series of substances like the di-carboxylic acids has also been attempted by a consideration of the surface groups likely to be produced in the interfacial adsorption layer.

37. On some of the physical properties of vitamine containing vegetable juices.

A. NAGARAJA RAO and C. ANANDARAMA RAO, Bangalore.

With the advent of the physico-chemical theories of biological processes the physical properties like surface tension, adsorption, and viscosity of various plant and vegetable juices assume greater importance in the elucidation of the rôle of vitamins in animal system. In this series of investigations the authors are engaged in the determination of the surface tension of fresh tomatoe and other vegetable juices and also the effect of temperature, dilution and ageing on the same.

Certain changes of the nature of an alteration in the acidity and the formation of some alcohols appear to be produced on the ageing of the juice, which are under further investigation.

38. Autocatalysis in coagulation.

S. S. JOSHI, Benares.

In view of the well-known limitations of the applicability of Smoluchowski's theory, a number of theories have been proposed during recent years for the kinetics of coagulation, which however are not free from difficulties. An examination of the available material shows that viscosity and turbidity constitute the principal source of the data for the coagulation kinetics. Evidence is now adduced to show that the *slow* coagulation is a markedly composite process, being the resultant of a series of changes, which correspond to discontinuities observed on viscosity-time curves, indicative of the progress of coagulation (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, 10, 329-340; Joshi and Nanjappa, *ibid.*, 1934, 11, 133-143; Joshi and Iyengar, *ibid.*, 1934, 11, 555-557). The value of such a property is a function of a number of (a) processes accessory to the main one, viz. coalescence of particles, which do not progress uniformly during coagulation. Evidence is also given for the (b) existence



of stages where the micellar and related changes are such as do not affect the property selected to measure coagulation. The operation of either of, or both (a) and (b) will give evidence of autocatalysis which is but spurious.

### 39. A proposed general theory for the kinetics of coagulation.

S. S. JOSHI, Benares.

Based on an extension of Freundlich's equation for the adsorption isotherm, the following equation has been deduced for the rate of coagulation in terms of  $\epsilon$ , the micellar charge,  $m$  the colloid concentration,  $C$ , the electrolyte concentration and  $a, n$ , which are constants.

$$\frac{dx}{dt} = ma(C - AC)^{\frac{\epsilon}{n}}.$$

It is found that Smoluchowski's general equation characteristic of the region of *rapid* coagulation (*Z. Phys. Chem.*, 1917, 92, 129) can be deduced as a particular case of the equation proposed. It also yields as another special case the well-known *empirical* equation of Paine (*Koll. Chem. Beih.*, 1912, 16, 430), and predicts the conditions under which the latter breaks down as also the corresponding sense of the drift of the 'Paine's constant'. A considerable amount of evidence has been obtained in these laboratories which shows that the effect of increasing the electrolyte concentration in increasing the rate of coagulation is *discontinuous*. This purely experimental finding is found to be deducible from the equation.

### 40. Coagulation of oil suspensions by mercury chloride solutions.

S. S. JOSHI and S. P. SARKAR, Benares.

This has been examined over a wide range of the normality of the above coagulant. The viscosity, turbidity, and the refractive index were measured during the coagulation; these showed the normal, familiar variations, the actual magnitude of the change being however small. As observed in numerous coagulations in these laboratories, the variation of viscosity was discontinuous with time; the nett increase in viscosity even after prolonged standing was but small in a large number of cases. Changes in the last two properties were confined to but initial stages. The observations of Joshi and Kulkarni reported elsewhere are considered as special to arsenious sulphide coagulations, and not a general characteristic of mercuric chloride as a coagulant.

### 41. Anomalous variations of viscosity and turbidity in the coagulation of arsenious sulphide by mercuric chloride solutions.

S. S. JOSHI and S. S. KULKARNI, Benares.

In a number of recent publications from these laboratories it has been shown that marked limitations exist in the use of viscosity change as a measure of the corresponding degree of coagulation. These limitations became conspicuous particularly in the use of *non-electrolytes* as coagulants. It was seen that some of the properties of mercuric chloride are characteristic of both the electrolytes and non-electrolytes. This and the fact that no quantitative information as regards its rôle as a coagulator is available in the literature suggested undertaking the present work. Distinct though slow coagulation of colloid  $\text{As}_2\text{S}_3$  was observed with concentrations as low as N/800. The last was raised to N/500



(when coagulation was very quick to appear) and the viscosity of the coagulating sol determined over long periods over a wide range of the coagulator and the colloid strengths. It was found that the viscosity of the system did not show any nett rise, even when the measurements were continued up to a stage, which produced appreciable flocculations. This is interesting since an appreciable increase of viscosity on coagulation is to be anticipated from the current theories of the viscosity of a colloid, as well as from the relevant data in the literature. .

Measurements were also made of the opacity of the coagulating sol with the same coagulant. The results were completely analogous to those on the viscosity, which is significant. It might be mentioned that the familiar variations of both the above properties were noticed when other coagulants were used.

42. Decomposition of sulphur dioxide in electric discharge ;  
variation of the ionization current during the reaction.

S. S. JOSHI and K. K. SARMA, Benares.

The reaction has been studied in the pressure range 4 to 15 cms. Hg in the annular space of the well-known Siemen's ozonizer due to potentials which were increased up to 16,000 volts (r.m.s.). The nature of the final products (viz. unchanged  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{O}_2$  and a peculiar white deposit the main part of which is sulphur) was independent of the applied voltage, the gas pressure and presumably of the frequency of the A.C. supply. An examination of a number of pressure-time curves showed that in general the course of the reaction was markedly composite. In the first stage of the decomposition the rate of change was slow. The duration of this stage increased by increasing the gas pressure at constant applied potential. This was followed by a short lived phase in which the reaction proceeded markedly rapidly, as judged by the diminution of the gas pressure in the system. The final section was always characterized by an exceedingly slow rate of change. On measuring the value of the ionization current flowing through the reaction vessel a remarkable correspondence was found to exist between the rate of the reaction and the corresponding current. In the first phase of the reaction mentioned already the current diminished fairly rapidly ; it then increased remarkably rapidly during the short interval, when a rapid diminution of pressure was produced ; the current was markedly low and nearly constant during the last stage of the decomposition. The close synchronousness between the current changes and those in the corresponding rate of decomposition is striking, and is in all probability related to the changing composition of the material in the ionization vessel. Evidence is adduced to show that even small quantities of sulphur trioxide possess a markedly depressant influence on the ionization of a gas subjected to an electric discharge.

43. Formation of molecular complexes in mixed solutions of  
potassium iodide and mercuric chloride.

S. S. JOSHI and K. K. SARMA, Benares.

A review of the literature on the subject showed that a very considerable amount of evidence exists to show that hydroxylation and especially association lead to appreciable increase in viscosity. The last quantity was measured for mixtures in which different amount of 0.1M,  $\text{HgCl}_2$  were added to solutions of potassium iodide. The proportion of the mercury chloride mixed with a given normality of the iodide solution was increased until precipitation of mercury iodide occurred. Measurements were made with 0.1M, 0.2M, and 0.3M KI solutions, at two temperatures, viz. 30°C. and 35°C. The curves relating the viscosity and the composition of the mixture showed a number of maxima and minima.



The positions of a number of these remained sensibly unaltered in the series mentioned above at the two temperatures. The occurrence of the maxima have been explained on the formation of complex compounds of the type  $(\text{HgCl}_2)_a(\text{KI})_b$  where  $a$  and  $b$  are constants.

44. Variation of viscosity during the slow coagulation of oil-in-water emulsions.

S. S. JOSHI and H. K. ACHARYA, Benares.

A review of the now considerable volume of data on the viscosity of colloids showed that but little quantitative information is available on the viscometric examination of the kinetics of the above type of emulsions. The present paper gives data for the coagulations of *Til*, Mustard, Linseed, and Paraffin oil emulsions. Various concentrated solutions of potassium bromide, potassium iodide, barium chloride, thallium chloride, and thorium nitrate were used as coagulants. It was observed that the progress of coagulation followed by viscosity measurements was markedly discontinuous, an appreciable diminution of viscosity being observed usually though not invariably at the commencement of the coagulation. Both these features disappear in rapid coagulations contrary to expectations from the current theories regarding the viscosity of a colloid and the usual experience, it was found that in a large number of coagulations, especially when low concentrations of thallium chloride and thorium nitrate are used viscosity of the coagulating system was markedly lower than its initial value.

45. Studies on the influence of electrolytes on the distribution of solutes between immiscible solvents. Part I—Partition of benzoic acid between toluene and water.

S. S. JOSHI and R. N. AMBIKE, Benares.

Results are given for the distribution coefficient of benzoic acid between the phases mentioned above in the presence of varying amounts of hydrochloric acid, lithium, sodium, potassium, rubidium, and ammonium chloride added to the aqueous phase. The constant diminishes by about 22 per cent. when the amount of the acid for example is increased up to 0.5N. Further increase up to 4N has no influence. The addition of the other chlorides (with the exception of ammonium chloride) in increasing amounts diminishes progressively the distribution constant. The first additions of ammonium chloride increase the coefficient to a maximum; subsequent additions lower its value analogous to other chlorides. Comparing the influence of the above chloride in diminishing the distribution coefficient, the order is  $\text{NaCl} > \text{KCl} > \text{RbCl} > \text{LiCl} > \text{HCl}$ . The thermodynamical theory of Nernst, the familiar salting out theory and that of the suppression of the ionization of benzoic acid have been shown to be inadequate to explain the observed results. The possible influence of the ionic hydration and especially of changes in the ionic activities and also that of the undissociated benzoic acid has been discussed.

46. Studies on the influence of electrolytes on the distribution of a solute between immiscible phases. Part II—The partition of iodine between toluene and water.

S. S. JOSHI and R. N. AMBIKE, Benares.

The influence of the addition of different amounts of KCl, LiCl, NaCl, HCl,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{SO}_4$  to the aqueous phase on the above distribution coefficient has been investigated. It has been found that



the constant diminishes by increasing the amount of any of the above substances, the effect being more pronounced in the first additions. The order of influence is  $K > Na > Li > H$  which is in part different from that observed in the benzoic acid distribution. As the amount of any of the four acids was varied progressively, it was found that the distribution constant diminished to a minimum (whose value depended upon the nature of the substance added), the influence of further additions being but insensible.

A detailed investigation was also made of the above distribution in the presence of potassium iodide in the aqueous phase, which leads to the formation of  $KI_3$  in water. The values of the equilibrium constant ( $KI \times I_2 / KI_3$ ) was studied in the presence of the foreign electrolytes mentioned above. The constant increases fairly rapidly as the concentration of  $LiCl$ ,  $KCl$ , and  $NaCl$  added is increased in the range 0 to 3N. Using acetic and nitric acids the constant increases up to a maximum at about 0.5N, and remains constant despite large increases in the amounts of the acids added.

#### 47. Nitrogen loss from soil in sunlight.

N. R. DHAR, S. P. TANDON, S. K. MUKERJI, and P. K. KAR,  
Allahabad.

In absence of oxygen and in presence of an easily oxidizable organic substance, many micro-organisms are capable of decomposing nitrates with the evolution of gaseous nitrous oxide or ammonia. This type of denitrification is well known. There is another variety of nitrogen loss, which takes place in presence of oxygen but has not yet been satisfactorily explained. In this paper it will be shown that this loss of nitrogen from the soil is due to an oxidation process followed by a photochemical and catalytic decomposition.

From the researches of J. G. Lipman and A. W. Blair carried on at New Jersey and California, it appears that nitrogen in the gaseous state is lost from soils when the conditions are favourable for oxidation. The loss amounted to 100 lbs. per acre per year in the first nine inches of the soil. In these experiments the conditions existing in the soil in the past were disturbed by making the soil suitable for more oxidation. Similar nitrogen losses have been observed at Rothamsted, Minnesota, Kansas, Indian Head (Saskatchewan), Allahabad, Nagpur, Coimbatore and other places. Nearly 70% of the added nitrogen is said to have been lost when wheat plots in Rothamsted have received 14 tons of farmyard manure containing 200 lbs. nitrogen. These losses are more pronounced in soils, which have been highly aerated.

That oxidation of ammonium salts is an important factor in this type of denitrification is also evident from the observations of Niklewski, who reported that when the manure was free from nitrifying bacteria, only 3% nitrogen was lost as ammonia but when supplied with nitrifying bacteria, the manure lost more than 20% of its nitrogen. Moreover, Russell and Richards have observed a greater loss of nitrogen when a manure was composted under aerobic than under anaerobic conditions. Vishwanath has observed that the greater the nitrate formation with different manures, the greater the nitrogen loss. It has been observed that the loss of nitrogen in presence of light is always greater and the oxidation is also greater than in the dark. Experiments carried on in different countries show that the total amount of nitrate lost from soils containing crop is greater than that in neighbouring fallow soils even when correction is applied for the amount of nitrate taken up by the crop.

Explanation on the foregoing observations on nitrogen loss are given in the paper.



## 48. Influence of temperature on fixation of nitrogen.

A. K. MALLIK and N. R. DHAR, Allahabad.

It is generally believed that nitrogen fixation takes place to a remarkable extent in tropical soils by free living bacteria. It seems that no systematic work has been done on this subject in this country. The writers have determined the nitrogen fixed at different temperatures by a pure culture of *Azotobacter* using the following medium :—

Distilled-water	..	..	..	1,000 c.c.
Mannite	..	..	..	15 gms.
K <sub>2</sub> HPO <sub>4</sub>	..	..	..	0.2 „
MgSO <sub>4</sub> , 7H <sub>2</sub> O	..	..	..	0.2 „
CaCl <sub>2</sub>	..	..	..	0.02 „
FeCl <sub>3</sub> one drop of 10 per cent. solution.				

It is well known that 90% of the nitrogen fixed is in the form of ammonia and hence we have determined the amounts of ammonia by Nessler's solution colorimetrically.

The results show that the amount of ammonia formed is highest at 35°; at 50° the amount of nitrogen fixed is exceedingly small. It seems therefore that in summer months in tropical countries when the soil temperature in many places exceeds 50°, very little nitrogen fixation by *Azotobacter* is possible.

## 49. Chemical reactivity and light absorption.

N. R. DHAR and P. N. BHARGAVA, Allahabad.

The writers have measured the light absorption of reducing agents like hydrogen, methyl alcohol, and ethyl alcohol vapour, and oxidizing agents like bromine and chlorine separately all in the gaseous state and in mixtures by photographing their absorption spectra with a Hilger Quartz Spectrograph E, employing copper and iron arc as the light source. The time of exposure was two minutes. The absorption chamber consisted of a tube 80 cms. long and 2.5 cms. in diameter. The pressures of bromine or chlorine and the reducing agents were 20 and 40 cms. Hg respectively.

From the results it is observed that the light absorption by a mixture of the reacting substances is greater than the absorptions by the ingredients considered separately. It is interesting to note that there is no increased light absorption when the gases or vapours are passed through concentrated sulphuric acid and phosphorus pentoxide. In other words, desiccation considerably decreases the chemical reactivity and prevents the combination of hydrogen and chlorine or hydrogen and bromine in the visible region. Hydrogen sensitizes the dissociation of chlorine and bromine molecules and makes them reactive in radiations of longer wavelengths only in the presence of moisture. These observations are supporting the important work of Baker who showed that intensive drying greatly reduces the reaction velocity of substances.

From numerous experiments carried on with solutions and the results obtained in this paper, it seems clear that if there is the possibility of the occurrence of a chemical change by mixing two or more substances increased light absorption is likely to be observed in those cases. We are of opinion that the increased light absorption by a mixture in comparison with those of ingredients is likely to be a measure of the reactivity of a given mixture of two or more substances.

## 50. Temperature and diamagnetism.

S. S. BHATNAGAR, M. B. NEVGI, and M. L. KHANNA, Lahore.

While trying the temperature effect on diamagnetism of some organic iodides the authors find that the diamagnetism of the iodides decreases



to some extent. This is quite contrary to the fact which was previously observed in the case of aromatic liquids. The results obtained so far are as follows :—

TABLE I.  
Ethyl iodide.

Temperature.	$-\chi \times 10^6$ .	% change.	Temperature coefficient.
15°C. 55°C.	0.4488 0.4356	2.94	0.00074

TABLE II.  
n-propyl iodide.

30°C. 70°C.	0.4958 0.4834	2.5	0.00063
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TABLE III.  
Phenyl iodide.

30°C. 70°C.	0.470 0.462	1.7	0.000425
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TABLE IV.  
o-iodo-toluene.

30°C. 70°C.	0.5145 0.5051	1.82	0.000457
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TABLE V.  
m-iodo-toluene.

30°C. 70°C.	0.5152 0.5065	1.7	0.000422
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It appears from the above results that iodine in the organic iodides might perhaps be responsible for the decrease in the diamagnetism of the organic iodides. Honda (*Ann. der Physik.*, 32, 1027, 1910) has shown that iodine increases in diamagnetism in solid state but decreases in the liquid state. The slight decrease in the diamagnetism of the iodides can be explained by the change in the diamagnetism of iodine at different temperatures. The above results are in the same direction. These results will be further extended and checked on the modified form of Decker's apparatus.



51. On the accurate measurement of diamagnetic susceptibilities.

S. S. BHATNAGAR, N. G. MITRA, and G. D. TULI, Lahore.

Pascal's classical data on the deduced values of  $\chi$  for atoms in combination is at its best a first approximation. An attempt has been made to repeat his work with the purest materials now available by taking measurements on the more sensitive Bhatnagar-Mathur Magnetic Interference Balance. The results obtained for hydrogen ( $\chi_H = -2.68 \times 10^{-6}$ ) and for chlorine ( $\chi_{Cl} = -19.85 \times 10^{-6}$ ) compare more favourably with the theoretical values derived on the wave mechanical concepts than the experimental values of Pascal.

52. Action of solvents in heterogeneous reactions. Part I—  
Effect on the velocity of reaction between carbon disulphide and alkali.

D. D. KARVÉ and K. K. DOLE, Poona.

Solutions of carbon disulphide in petroleum ether and in xylene were shaken with varying quantities and concentrations of sodium hydroxide and the sulphur in the aqueous layer was estimated after one hour. It was found that the extent of reaction is greater with xylene than in petroleum ether, although in both solvents it is seen to increase proportionately with concentration.

53. Action of solvents in heterogeneous reactions: Part I.  
Effect on the velocity of reaction between benzoyl chloride and water.

D. D. KARVÉ and K. K. DOLE, Poona.

The velocity of the reaction between benzoyl chloride and water was determined when carbon disulphide, chloroform, carbon tetrachloride, chlorobenzene, bromobenzene, and xylene were used as solvents for the former. The extent of reaction in a given time was greatest with  $CCl_4$ , and went on diminishing in the order: Carbon tetrachloride, xylene, carbon disulphide, chlorobenzene, bromobenzene, and chloroform. Besides the physical properties like viscosity and density, various others like surface tension, dielectric constant, etc. seem to determine this effect on the speed of a heterogeneous reaction.

54. On some critical aspects of adsorption.

A. GANGULI, Chandernagore.

Recent quantum-mechanical dispersion theory shows that there is no appreciable difference between the old capillary condensation, surface orientation, potential, and electrical theories. Adsorption forces originating from electrical polarisation are identified with van der Waal forces operative in condensation and regarded as residual valence forces. Activated adsorption however involves a mechanism of activation as in chemical kinetics. But some explain this as due to slow diffusion or of removal of impurities adhering to the surface.

In order to understand mechanism of adsorption further experiments on the structure, extent, purity and thickness of surface layer are required. Roughness of surface and cracks of Smekal tracks may account for the difference in the actual and theoretical values of adsorption potential and diffusion. Again adsorption is sometimes accompanied by swelling. Activation of adsorbents consists essentially of removal of impurities



(causing increase in adsorption), increase of surface (formation of single crystals), and development of cracks. It is rational to express adsorption per unit surface rather than per unit mass of adsorbent and these are not always identical. Kinetics and energetics of adsorption at different temperatures should be carefully studied. At low temperatures owing to slow vibrations, molecules are held atom by atom to the adsorption centres while with rise in temperature some linkages break away. This accounts for difference in adsorption.

55. Conductometric studies of stearic acid hydrosols : Part II.

M. P. VENKATARAMA IYER and B. SANJIVA RAO, Bangalore.

Stearic acid sols offer one of the simplest and at the same interesting systems, which can be studied electrometrically, and conclusions drawn regarding the nature of the interfacial layer and reactions at interfaces. In continuation of the work described by one of us (*Proc. Indian Science Congress, 1932 : J. Mys. University, 1932*) we have carried out measurements of the conductivity of Stearic acid sols and its variation with dilution. Conductometric titrations of the sol against Sodium and Barium hydroxides respectively have also been carried out. The results fully support the theory proposed by the author in previous papers (*J. Ind. Chem. Soc.*, 8, 613, 1931; *J. Mys. University, loc. cit.*) that the 'adsorption theory' with modifications involving 'deformation' of ions can satisfactorily explain all observed facts.

56. Mechanism of the clarification of muddy water by strychnos potatorum seed-paste.

B. SANJIVA RAO and K. SUBBARAMIAH, Bangalore.

Clarification of water by the paste from the seeds of *Strychnos potatorum* has usually been attributed to the proteins in the seeds. Investigations by the authors show that the proteins merely sensitize the suspension and that the actual precipitation is effected by the actions of the alkaloid.

57. The E.M.F. of the system  $\text{Hg}/\text{HgO}/\text{Stad. Ca(OH)}_2$ .

K. SUBBARAMIAH and B. SANJIVA RAO, Bangalore.

The E.M.F. of the above system has been shown to be steady and reproducible and to have the value  $0.2023 - 0.00035(t-30)$  with respect to the N-Hydrogen electrode. It is offered as a convenient standard alkaline electrode for the potentiometric estimation of copper ions in Bordeaux mixture.

58. Investigations on Vitamin C.

A. R. GHOSH and B. C. GUHA, Calcutta.

The content of Vitamin C (ascorbic acid) in different Indian food-stuffs has been determined by the titration technique with 2 : 6—dichlorophenol—indophenol. Pineapple, lichies, and red pepper appear to be the richest sources.

Experiments have been carried out on the production of Vitamin C *in vitro* from carbohydrates in the presence of the tissues of the rat. Some carbohydrates appear to show specific behaviour in this respect.



59. Studies on flavins from ox-kidney and *mator* (*Pisum Arvense*).

H. G. BISWAS and B. C. GUHA, Calcutta.

Attempts have been made to isolate a flavin from ox-kidney (renoflavin) and one from *mator* (*Pisum Arvense*) by employing methods, developed by Kuhn. Both the flavins have physiological activity, in that they can promote growth in young Vitamin B<sub>2</sub>-deficient rats. The order of activity has, however, not yet been finally determined.

60. The biological oxidation of inositol.

N. DAS and B. C. GUHA, Calcutta.

Studies on the oxidation of inositol by the brain, kidney, heart muscle, and liver tissues of the rat were carried out. The Barcroft-Warburg microrespirometer was used and the tissues were suspended in a mixture of phosphate buffer at pH 7.4 and Ringer-Locke solution. Inositol was found to be oxidized by all the tissues. The rate of respiration with liver tissue was the lowest.

61. Vitamin A in Indian fish-liver oils.

A. R. GHOSH and B. C. GUHA, Calcutta.

Further studies on the above subject indicate some disparity between the biological and tintometric values of some Indian fish-liver oils.

62. Dyes derived from phenanthraquinone.

P. C. DUTTA and DAMODAR PRASAD, Mazafferpur.

6-Chloro-3.4-tolylene diamine (Morgan and Drew, *J.C.S.*, 1920, 117, 784) was condensed by the authors with various derivatives of phenanthraquinone and thereby yellow or brown azine dyes obtained (*Proc. Indian Science Congress*, 1934). In the azine dyes, the chromophoric property of the azine ring is enhanced by the change of a nitrogen atom from the trivalent to the pentavalent condition or in other words by the conversion of the azine to an azonium compound. The present communication deals with compounds of the flavinduline type obtained by condensing 6-chloro-3-phenyl-3.4-tolylene diamine (Morgan and Jones, 1921, 119, 191) with phenanthraquinone and its various derivatives in acetic acid solution in presence of conc. hydrochloric acid. As expected, these compounds are all much deeper in colour than similar compounds of the azine type. The 2-amino-phenanthraquinone condensed product is a violet dye and most of the other compounds are deep chocolate in colour. These compounds dissolve in conc. sulphuric acid with a pink colour.

63. Studies in indigoid dyes. Part VIII. 1.8-peri-naphthathiophene-phenanthrene-indigos.

P. C. DUTTA, Mazafferpur.

The author has been studying the relation between colour and chemical constitution of the naphthathiophene-phenanthrene-indigos. 1.2-, 2.1-, and 2.3-naphthathiophene-phenanthrene-indigos have already been described in parts II, IV, and VI respectively (*Ber.*, 1933, 66, 1226; *ibid.*, 1934, 67, 5, 1319). The present paper deals with 1.8-peri-naphthathiophene-phenanthrene-indigos obtained by condensing 1.8-naphthoxy-penthiophene with phenanthraquinone and its various derivatives and completes all the possible naphthathiophene-phenanthrene-indigos.



Unlike the isomerides already described, these compounds are slightly soluble in alkaline hydrosulphite vat and as such the shades obtained on cotton are rather light. The 2-aminophenanthraquinone condensed product dyes cotton in pure green shade from the vat and the other compounds mostly in violet shade.

#### 64. Studies in indigoid dyes.

S. K. GUHA, Patna.

It has been shown by Guha (*J. Ind. Chem. Soc.*, 1933, 10, 679) and Guha and Mullik (*ibid.*, 1934, 11, 395) that 5-methyl-3-hydroxy-thionaphthene (Auwers and Arndt, *Ber.*, 1909, 42, 541) reacts readily with aromatic 1 : 2 diketones such as acenaphthenequinone, isatin and their various derivatives and phenanthraquinone, giving rise to beautiful indigoid vat dyes which impart a deeper shade on wool as well as on cotton than those of the corresponding compounds obtained from 3-hydroxy-thionaphthene (*cf.* Bezdik and Friedlander, *Monatsh.*, 1908, 29, 306 and 376; Guha, *J. Ind. Chem. Soc.*, 1932, 9, 423). This paper describes the preparation and properties of more of indigoid compounds obtained from 5-methyl-3-hydroxy-thionaphthene and various aldehydes such as glyoxal, *p*-chlorobenzaldehyde, anisaldehyde, piperonal, vanillin, cinnaminaldehyde, protocatechuicaldehyde, *m*-nitrobenzaldehyde, *p*-hydroxybenzaldehyde, *p*-dimethyl-aminobenzaldehyde, and *m*-aminobenzaldehyde. (*cf.* Auwers and Arndt, *loc. cit.*).

#### 65. Dyes derived from acenaphthenequinone. Part V. Indigoid vat dyes.

S. K. GUHA, Patna.

Friedlander and Woroshzow (*Annalen*, 1912, 388, 1) observed that of the four naphthothiophene-indigos, the bis-1 : 8-derivative is pure blue. This led the author to think that if 1 : 8-naphthothiooxypenthiophene could be condensed with acenaphthenequinone and its various derivatives, the resulting naphthopenthiophenacenaphthylene indigos might possess deep colour. With this object in view 1 : 8-naphthooxypenthiophene (Friedlander and Woroshzow, *loc. cit.*) was condensed with acenaphthenequinone, 3-chloro-, 3-bromo-3-methoxy and its 3-4-dinitro derivative only. The expectations have not been realised. These compounds are deep red substances. The analogously composed phenanthraquinone derivative has also been obtained which is dark chocolate.

#### 66. The estimation of phenylmercaptan.

BALWANT SINGH, ANAND SARUP, and H. B. DUNNICLIFF, Lahore.

Copper sulphate has been used as a reagent to estimate phenyl mercaptan in benzene solution. For comparison the amount of phenyl mercaptan in the benzene solution was also determined by treatment with mercuric chloride (Sampey and Reid, *J. Amer. Chem. Soc.*, 1932, 54, 3404). The acid liberated in each case was titrated with a standard solution of sodium hydroxide and the end point determined by a conductometric method.

#### 67. Studies on optical activity and chemical constitution. Optically active acids and bases. Part I. The condensation products of *m* and *p*-amino dimethylanilines with camphoric anhydride.

MAHAN SINGH and H. B. DUNNICLIFF, Lahore.

*p*-Dimethylaminophenylimino-camphor has very high rotatory power. In aniline it is  $(\alpha)_D = 3000^\circ$  and  $(\alpha)_{5780} = 3344^\circ$ . This value



exceeds those of the compounds prepared by Forster and Thornley (*J.C.S.*, 1909, 95, 942), Singh and Singh (*J.C.S.*, 1921, 119, 789), and Patel and Guha (*J.I.C.S.*, 1934, 9, 987), though the compound under discussion does not possess the essentials of these compounds. This remarkable effect of the dimethylamino group has also been recorded by Betti (*Gazetta Chim. Ital.*, 1923, 53, 424) in the condensation product of  $\alpha$ -naphtholbenzylamine with *p*-dimethylaminobenzaldehyde.

While the rotations of acids and bases fall or are reversed in sign when they are ionized, the rotation of dimethyl-amino hydrochloride in ethyl alcohol is  $(\alpha)_D = -53^\circ$  while that of the base is  $(\alpha)_D = 2486^\circ$ . This compound is both thermotropic and phototropic.

*m*-Dimethylaminophenylimino camphor has  $(\alpha)_D = 711^\circ$  (aniline).

68. Studies on optical activity and chemical constitution. Optically active acids and bases. Part II. The condensation products of *o*-, *m*- and *p*-aminodimethylanilines with camphoric anhydride.

MAHAN SINGH and H. B. DUNNICLIFF, Lahore.

*o*-Dimethylaminocamphoranilic acid (m.p.  $153^\circ$ ) has a very small positive rotation. The dimethylamino group is known to have a depressing effect in the *o*-position (cf. Rule and co-workers, *J.C.S.*, 1926, 553, 2116; 1928, 178; 1929, 401, 2274). This substance is an optically active amino acid, in which three phases are possible; the ionized carboxylate, the free amino acid and the ionized amino compound. The substance was therefore examined, first in the presence of an equivalent amount of alkali and secondly with an equivalent amount of hydrochloric acid. It has a slight + rotation in a neutral medium, which increased very little when alkali was added, but  $(\alpha)_D$  rose to  $55.5^\circ$  when an equivalent weight of the acid was present; (cf. *d*-aspartic acid behaves similarly).

The dimethylamino group in the *p*-position produces an exaltation but not to the extent that was expected. *p*-Dimethylamino camphoranilic acid (m. p.  $193^\circ$ ) obeys the simple dispersion formula of Drude  $\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$  but the rotatory dispersion of the *o*-dimethylaminocamphoranilic acid is complex.

69. The physical identity of enantiomers. Part I. Rotatory dispersion of enantiomeric borneols, camphors, camphoric acids, sodium camphorates and camphoric anhydrides.

B. K. SINGH and INDRAMANI MAHANTI, Cuttuck.

Last year a preliminary account of the work was given. The authors have now made a complete study of the rotatory dispersion of *l*-borneol in ethyl alcohol and benzene, *d*- and *l*-camphor in ethyl alcohol, benzene and acetone, *d*- and *l*-camphoric acid in ethyl alcohol, acetone and water, *d*- and *l*-sodium camphorate in water, and *d*- and *l*-camphoric anhydride in ethyl alcohol and chloroform for 10 different wavelengths ( $\lambda = 4358$  to  $6709$ ). They have shown that the claim of Campbell (*J. Amer. Chem. Soc.*, 1930, 26, 560; 1931, 53, 1661) that there are differences in the numerical values of the rotatory power of *d*- and *l*-camphoric acids, cannot be substantiated. On the other hand, they find that there are no differences in the rotatory power of optically active and opposite forms. It is clear that the samples with which Campbell worked, were impure.



Another case of *d*- and *l*-mandelic acid which is also cited by Campbell as not obeying Pasteur's Law of Molecular Dissymmetry has been shown by Körtum (*Ber.*, 1931, 64B, 1506) to be due to impure samples of the acids. With the satisfactory removal of discrepancies noticed in the case of mandelic and camphoric acids, it may now be asserted that Pasteur's Law of Molecular Dissymmetry rests on sound experimental basis.

#### 70. Synthetical experiments on Genkwanin and Wogonin.

K. C. GULATI and K. VENKATARAMAN, Lahore.

Bharadwaj and one of the writers have shown that 5-hydroxy-flavones can be prepared by the action of aluminium chloride on the 5-methyl ether; a new synthesis of tectochrysin was carried out by this method. The writers have now found that by the regulated action of aluminium chloride chrysin dimethyl ether and tectochrysin can be directly prepared from 2 : 4 : 6-trimethoxydibenzoylmethane. An alternative route to chrysin dimethyl ether has been found in the action of sodamide on 2-benzoyloxy-4 : 6-dimethoxyacetophenone. The synthesis of genkwanin (5 : 4'-dihydroxy-7-methoxyflavone) and wogonin (5 : 7-dihydroxy-8-methoxyflavone) by means of these reactions is nearing completion.

#### 71. The constitution of bilobetin.

K. C. GULATI, H. S. MAHAL, and K. VENKATARAMAN, Lahore.

Comparison of the properties of 3 : 7 : 4'-trihydroxyflavone, prepared by the Robinson reaction, with those of demethylbilobetin has revealed their non-identity, a conclusion also arrived at by Furukawa by degradation experiments on the natural substance. The correctness of Furukawa's suggestion that bilobetin is a methyl ether of 5 : 8 : 4'-trihydroxyflavone is being tested by synthesis of the 5 : 8-dihydroxyflavone type. After unsuccessful attempts to prepare 2-hydroxy-3 : 6-dimethoxyacetophenone, we have resorted to the conversion of 5-benzeneazo-8-hydroxyflavone through the obvious stages to 5 : 8-dihydroxyflavone.

#### 72. Antiseptics and anthelminthics : the naphthalene analogue of thymol.

K. B. SEHRA and K. VENKATARAMAN, Lahore.

1-Methyl-4-isopropyl-3-naphthol, being a derivative of thymol and of  $\beta$ -naphthol, may be anticipated to have interesting physiological properties and progress towards its synthesis is described. Thymol methyl ether, succinic anhydride and aluminium chloride gave 2-methyl-4-methoxy-5-isopropyl-benzoylpropionic acid; Clemmensen reduction yielded the  $\gamma$ -phenylbutyric acid, which did not undergo ring closure to the ketotetrahydronaphthalene. Alternative processes, such as the action of aluminium chloride on 1-methyl-3-naphthyl isopropyl ether, are being investigated. The paper includes the preparation of certain new antiseptics derived from trichlorophenol, tribromophenol and  $\beta$ -naphthol.

#### 73. Antiseptics and anthelminthics : C-benzylflavones.

K. C. GULATI, K. B. SEHRA, and K. VENKATARAMAN, Lahore.

Having encountered in the leaves of *Calycopteris floribunda* a flavone with anthelminthic properties (paper communicated to the *Biochemical Journal*), an examination of other flavones from this point of view has been instituted. Since C-benzylphenols are known to have antiseptic



properties we have prepared certain C-benzyl hydroxyflavones; the latter have an additional interest as the natural colouring matters, garcinin and fukugetin, have recently been shown to belong to this type. The sodamide reaction, evolved by Mahal and one of us, on 2-benzoyloxy-4-benzyloxyacetophenone gave 2-hydroxy-4-benzyloxydibenzoylmethane (I) or 2-hydroxy-7-benzyloxyflavanone, (II) according to conditions, both being convertible into 7-benzyloxyflavone, (III) and 7-hydroxyflavone. The interaction of (III) with aluminium chloride resulted in 8-benzyl-7-hydroxyflavone; the 6-benzyl isomer was obtainable from 5-benzyl-resacetophenone, prepared by a Hoesch reaction on C-benzylresorcinol.

#### 74. The action of sodamide on *o*-acyloxyacetophenones.

D. C. BHALLA, H. S. MAHAL, and K. VENKATARAMAN,  
Lahore.

It has been shown by two of us elsewhere (*Current Science*, 1933) that 2-acetyl-1-naphthyl benzoate in ether is smoothly converted by sodamide at room temperature to 2-benzoylacetyl-1-naphthol, closure of which to  $\alpha$ -naphthaflavone can be effected by the usual methods. In view of the significance of this observation for determining the course of the Robinson reaction and for the synthesis of natural colouring matters of the flavone group, we have studied the action of sodamide on the *o*-acyl derivatives of numerous other ketones, such as *o*-hydroxyacetophenone, 1-acetyl-2-naphthol, *w*-methoxyresacetophenone and 2-phenylacetyl-1-naphthol; the acyl derivatives included the acetyl, benzoyl, anisoyl and cinnamoyl. The behaviour was of four types: (1) no reaction took place and the original ketone was recovered; (2) the diketone was produced; (3) the product was the 2-hydroxy-2 : 3-dihydro- $\gamma$ -pyrone; (4) the chromone was directly obtained.

#### 75. Detergency of soap solutions.

B. G. ACHARYA and T. S. WHEELER, Bombay.

The object of the work is to determine the amount of soap absorbed by cotton from dilute solutions of neutral soaps prepared from various oils and fats. From the relative absorption of various soaps on yarns, the exact concentration and temperature at which a particular soap has its maximum detergency is deduced. On addition of varying amounts of soap-builders, like sodium carbonate, tri-sodium phosphate, sodium silicate, and borax to different soap solutions, the amount of absorption by the yarns is noted and from the data the exact proportion of the builder giving the maximum scouring effect is deduced. Further the effect of absorption by the addition of sodium chloride is also studied.

Surface-tension, viscosity and pH measurements are being carried out with the above solutions to see if a relation exists between the absorption values and these properties.

#### 76. The reactions of acetophenone-piperonal.

R. P. DODWADMATH and T. S. WHEELER, Bombay.

The above chalkone was oxidised by means of  $H_2O_2$  in presence of an alkali to the *oxide* (m.p.  $97-8^\circ$ ) which reacts with methyl alcohol in presence of  $H_2SO_4$  to give a *methoxy-compound* (m.p.  $117-8^\circ$ ) and with ethyl alcohol to give an *ethoxy-compound* (m.p.  $93-4^\circ$ ). The oxide condenses with  $NH_2NH_2$  to give a *hydrazone* (m.p.  $172-3^\circ$ ), which further changes to a *pyrazole* (m.p.  $194-5^\circ$ ). On boiling the methoxy compound with a few drops of aqueous alkali a *diketone* (m.p.  $111-3^\circ$ ) is obtained which condenses with *o*-phenylene-diamine to give a *quinoxaline-compound* (m.p.  $136-8^\circ$ ). The oxide with alcoholic alkali is converted into a *glycollic acid* (m.p.  $149-50^\circ$ ), the diketone being first formed. The



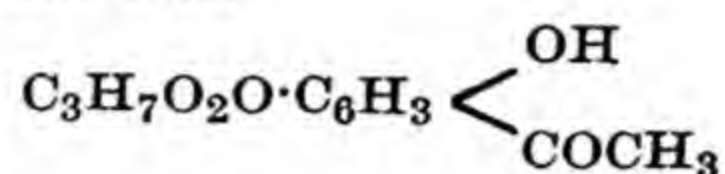
chalkone also gives a *dibromide* (m.p. 153-4°) and a *tribromide* (m.p. 172-3°). The dibromide when boiled with methyl alcohol gives a *mono-bromo-monomethoxy-compound* (m.p. 115-6°) and with ethyl alcohol gives a *monobromomonoethoxy-compound* (m.p. 143-4°). Similarly a *monochloro-monomethoxy* and a *monochloro-monoethoxy compound* (m.p. 118-9°) have been prepared. A *trichloride* (m.p. 127-8°) of the chalkone has been isolated.

Similar reactions have been carried out with acetophenonenitropiperonal.

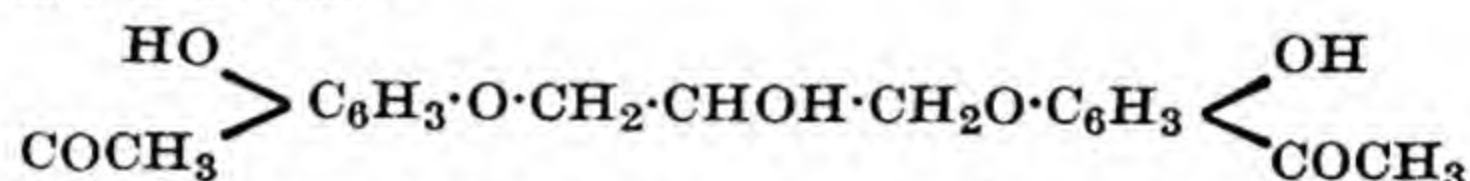
### 77. Condensation of glyceryl chlorhydrin with resacetophenone.

D. R. NADKARNI and T. S. WHEELER, Bombay.

Two products, a *mono-ether*



and the other a *di-ether*



were obtained from the above condensation. The latter was confirmed by preparing it from epichlorhydrin which also gave the *glycide ether* under different conditions.

These ethers condense with several aldehydes to give the respective *chalkones* of which the *tri-bromo derivatives* give on hydrolysis *bromo-flavones*, the *di-bromo* obtained from the *acetoxy-chalkones* also give *flavones*.

The chalkones from the mono-ether give *flavonols* with 6 % hydrogen peroxide in 30 % yield, while those from the di-ether give only with 30 % hydrogen peroxide.

### 78. Condensation of benzotrichloride with nitranilines.

A. P. KHANOLKAR and T. S. WHEELER, Bombay.

Benzotrichloride was condensed with *p*-nitraniline in nitrobenzene and *di*-(*p*-nitro-phenyl) benzamidin, m.p. 191° was obtained in the form of its hydrochloride. Its *acetyl* and *benzoyl* derivatives have m.p. 181-83° and 198° respectively. With chloro-formic ester a *compound* of m.p. 168° was obtained. With benzanilideimidochloride it gave a *compound* m.p. 142-144°. On oxidation with H<sub>2</sub>SO<sub>4</sub> and KMnO<sub>4</sub> it gave a *compound* m.p. 234-235° of which the probable constitution is [C<sub>6</sub>H<sub>5</sub>C( : NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>) (·NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)]<sub>2</sub>.

A similar condensation was obtained with *m*-nitraniline and the same reactions carried out with the product obtained. *o*-nitraniline also gave a condensation product but the yield was small.

The synthesis of *di*-(*p*-nitro-phenyl)benzamidin from benz-*p*-nitraniline imido chloride and *p*-nitraniline is being effected.

### 79. Condensations of benzotrichloride.

S. P. JOSHI and T. S. WHEELER, Bombay.

*s*-Tribromophenol on condensation with benzotrichloride yields a *compound* (m.p. 102°) insoluble in acids and alkali, which appears to have the constitution: C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>Br<sub>6</sub>. Further work is in progress. *p*-Chloroaniline on condensation with benzotrichloride in nitrobenzene as medium yields *di*-(*p*-chlor-phenyl)-benzamidine (m.p. 142°) as the *hydrochloride*. It has been *acetylated* and *benzoylated*. *s*-Tribromoaniline similarly gives an *amidine* (m.p. 192°-93°).



80. Kinetics of heterogeneous organic reactions: the reactions between organic halogen compounds and solid inorganic salts.

M. V. NABAR and T. S. WHEELER, Bombay.

It has been found that ethyl ether inhibits the reaction between benzyl chloride and silver nitrate, the effect being quite apparent when 2% of ether is added to benzyl chloride.

The rate of reaction is proportional to the quantity of silver nitrate and to the concentration of benzyl chloride in the mixture of benzyl chloride and ether. In other words the reaction occurs at the surface of the silver nitrate and not throughout the solution.

Carbon tetrachloride decreases the rate of reaction but not to the same extent as ether. The presence of water greatly decreases the rate of reaction.

81. Effect of inhibitors on the benzoin reaction.

B. F. FERREIRA and T. S. WHEELER, Bombay.

The action of various inhibitors on the benzoin reaction is being studied. Sulphur is found to be the most powerful, 1 part in 20,000 being sufficient to produce a marked depression in the normal yield. Carbon bisulphide also inhibits the reaction but to a lesser extent, 1 part in 200 being sufficient to lower the normal yield.

The curves obtained are of the same type as those obtained with pure potassium cyanide, with this difference, however, that a diminished quantity of KCN appears to be functioning in the heterogeneous reaction. The homogeneous autocatalytic reaction is unaffected.

It is intended to try the effect of other inhibitors like  $H_2S$ ,  $SO_2$ , and organic compounds of sulphur.

82. Kinetics of the benzoin reaction in the presence of solvents.

P. S. REGE and T. S. WHEELER, Bombay.

Previous work in this laboratory on the kinetics of the reaction has been extended to a study of the effect of solvents. Toluene and chlorobenzene have been found to act as inhibitors. The results can be explained on the assumption that they precipitate potassium cyanide from its solution in benzaldehyde. Ethylene glycoll has a marked accelerating effect.

83. Reactivity of formic acid.

L. S. HEBLE and T. S. WHEELER, Bombay.

It has been found that anhydrous formic acid reacts with compounds containing a reactive halogen atom replacing it with a hydroxyl group and forming HCl and CO. Benzotrichloride and benzal chloride treated in this way are converted quantitatively to benzoic acid and benzaldehyde respectively. Reaction also occurs with benzyl chloride but the reaction is slow except in presence of zinc chloride. Acetyl chloride reacts violently at ordinary temperature with formic acid, and benzoyl chloride somewhat more slowly. The reaction can be applied to the quantitative estimation of reactive halogen, the hydrogen chloride evolved being absorbed in silver nitrate.

84. Some reactions of 2-phenyl-4-hydroxy-3-carbethoxy-quinoline.

R. C. SHAH and V. R. HEERAMANNECK, Bombay.

2-Phenyl-4-hydroxy-3-carbethoxy-quinoline, obtained through the condensation of benzanilide-imido-chloride, and sodio-ethyl-malonate



was hydrolysed to the free acid, and this has been smoothly decarboxylated to the known 2-phenyl-4-hydroxyquinoline, m.p.  $254^{\circ}$ , by heating with water in a sealed tube at  $210-220^{\circ}$ . Heating at a lower temperature ( $160-170^{\circ}$ ) with water gives a compound, m.p.  $218-220^{\circ}$ , which appears to be a dimorphic modification of 2-phenyl-4-hydroxy-quinoline.

Action of phosphorus pentachloride on the carbethoxy-quinoline gives the corresponding 4-chloro-derivative, m.p.  $101-103^{\circ}$ , in which the chlorine atom is shown to be mobile by its ready conversion by hydrolysis into 2-phenyl-4-hydroxy-quinoline-3-carboxylic acid.

It is found that the carbethoxyquinoline does not give a colouration with alcoholic ferric chloride nor does it absorb bromine. It is, therefore, concluded that it has the ketonic constitution of 2-phenyl-3 : 4-dihydro-3-carbethoxy-4-quinolone.

Ethylation by sodium ethoxide and ethyl iodide gives a C-ethyl derivative, m.p.  $226-228^{\circ}$ , whose constitution as 2-phenyl-3 : 4 dihydro-3 ethyl-3 carbethoxy-4-quinolone follows from the fact that it is identical with the compound obtained through the condensation of benzanilideimido-chloride with the sodium compound of ethyl-malonic ester. Methylation in a similar manner gives the C-methyl derivative, m.p.  $165-166^{\circ}$ .

### 85. Chemistry of imido-chlorides. Part V. Reaction of benzanilide-imido-chloride with aromatic tertiary amines. Geometrical isomerism in the amidines.

R. C. SHAH and R. V. SHAH, Bombay.

Shah, Despande, and Chaubal made the observation that benzanilide-imido-chloride reacts at a higher temperature with dimethylaniline and diethylaniline to give crystalline bases  $C_{20}H_{18}N_2$  (m.p.  $148-150^{\circ}$ ) and  $C_{21}H_{20}N_2$  (m.p.  $150^{\circ}$ ) respectively, the condensation taking place at the nitrogen atom with the elimination of alkyl halide.

The constitutions  $Ph-C \begin{smallmatrix} \nearrow NPh \\ \searrow N-Me \end{smallmatrix}$  and  $Ph-C \begin{smallmatrix} \nearrow NPh \\ \searrow N-Et \end{smallmatrix}$  were assigned

to the two compounds, which, however, were found to be not identical with the products obtained from benzanilide imido-chloride and monomethylaniline and monoethylaniline respectively. The non-identity was provisionally explained as being due to geometrical isomerism due to C=N linkage.

The study has been continued and it has been found that benzanilide-imido-chloride reacts with dimethylaniline at a lower temperature to give the oily base, identical with the one obtained from monomethylaniline; whereas at higher temperatures, it gives the solid isomer, m.p.  $148-150^{\circ}$ . At intermediate temperatures a mixture of the oily and solid isomers is obtained and a method has been worked out for the complete separation of the isomers. It thus appears that the oily base is first formed and then undergoes isomerisation to the solid base at a higher temperature.

The constitution assigned to the solid base, m.p.  $148-150^{\circ}$ , from benzanilide-imido-chloride and dimethylaniline has been confirmed by hydrolysis with concentrated hydrochloric acid in a sealed tube at  $150-160^{\circ}$ , when the products obtained were identified as benzoic acid, aniline, and monomethylaniline. It is thus definitely proved that both the solid

and the oily bases have the same constitution  $Ph-C \begin{smallmatrix} \nearrow NPh \\ \searrow N-MePh \end{smallmatrix}$  and the

isomerism must, therefore, be geometrical isomerism as suggested before. The observation is of great interest as this is the first case of geometrical isomerism in the amidines.



86. Chemistry of imidochlorides. Part VI. Reaction of benzanilide-imido-chloride with monohydric phenols in the presence of anhydrous aluminium chloride: A synthesis of hydroxybenzophenones.

R. C. SHAH and M. C. LAIWALLA, Bombay.

In continuation of previous work of one of the authors (Shah, *Proc. Indian Science Congress*, Bombay, 1934) the authors have condensed benzanilide-imidochloride with phenol in the presence of anhydrous aluminium chloride. The product obtained in good yield, is the anil of *p*-hydroxybenzophenone which hydrolyses readily by aqueous alcoholic hydrochloric acid to give the free ketone. This provides a convenient method for the preparation *p*-hydroxybenzophenone. The study is being extended to cresols and substituted phenols.

87. Chemistry of imidochlorides. Part VII: derivatives of *N*-phenylbenzamidine.

R. C. SHAH and H. P. GHADIALI, Bombay.

*N*-Phenylbenzamidine  $\text{Ph}-\text{C} \begin{smallmatrix} \text{= NPh} \\ \text{\textbackslash NH}_2 \end{smallmatrix}$  or  $\text{Ph}-\text{C} \begin{smallmatrix} \text{< NHPH} \\ \text{\textbackslash NH} \end{smallmatrix}$ , m.p. 112°, has

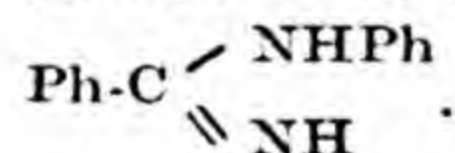
been previously prepared in poor yields (about 20%) by shaking a solution of benzanilideimidochloride in petroleum ether with concentrated aqueous ammonia.

The amidine has now been prepared in about 80% yield by a modified method, in which a solution of benzanilideimidochloride in dry ether is added to an excess of methyl alcoholic ammonia. With an excess of ben-

zanilide imidochloride, the dicondensation product  $\text{Ph}-\text{C} \begin{smallmatrix} \text{= NPh} \\ \text{\textbackslash NH-C} \end{smallmatrix} \begin{smallmatrix} \text{< Ph} \\ \text{\textbackslash NPh} \end{smallmatrix}$

M.P. 174° which is new, is obtained.

Several reactions of the amidine have been studied, including those with benzaldehyde, phenylisocyanate, urethane, and  $\alpha$ -naphthylisocyanate, and chloracetic ester and definite crystalline products isolated in all cases. In most of these the amidine appears to react in the form



Acetyl and benzoyl derivatives of the amidine have been prepared and the action of dehydrating agents on these will be studied in the expectation of converting them into derivatives of 4-methyl and 4-phenyl-quinazolines.

88. C-alkyl resorcinols. Part V. A new and simple synthesis of rhizonaldehyde.

R. C. SHAH and B. V. SAMANT, Bombay.

Rhizonaldehyde, -2-hydroxy-4-methoxy-3 : 6-dimethylbenzaldehyde, which is related to rhizonic acid, a lichen acid, -2-hydroxy-4-methoxy-3 : 6-dimethyl benzoic acid, has been previously synthesised from  $\beta$ -orcinol, 2 : 5-dimethyl-resorcinol itself obtained from *p*-xylylene through a number of stages (Sönn, *Ber.*, 1916, 49, 2589; Robertson, *J.*, 1930, p. 313, Pfau, *Helv. Chim. Acta*, 1928, 2, 864).

The authors have now achieved a simple synthesis of rhizonaldehyde directly from orcinol. Orcylaldehyde, prepared from orcinol, when



methyated by KOH and  $\text{CH}_3\text{I}$  under special conditions, undergoes nuclear methylation and directly gives rhizonaldehyde, m.p.  $136^\circ$ . Sönn and Pfau give m.p.  $136^\circ$ . It gives a reddish brown colouration to alcoholic ferric chloride.

### 89. C-Alkyresorcinols. Part IV. Synthesis of polyalkyl-resorcinols.

R. C. SHAH and P. R. MEHTA, Bombay.

In continuation of previous work, already reported to the Chemistry Section of the Indian Science Congress, Bombay (1934), the authors have synthesised some more polyalkyl resorcinols. 4 : 6-Diethyl resorcinol did not undergo the Hoesch reaction to give the 2-acetyl derivative, but the preparation of the corresponding aldehyde, 3 : 5-diethyl-2 : 6-dihydroxy-benzaldehyde could be achieved, and this on reduction by the Clemmensen method gave 4 : 6-diethyl-2-methyl-resorcinol.

Orsacetophenone was reduced similarly to give 4-ethyl-5-methyl resorcinol. Hoesch reaction on the latter gave 4-ethyl-5-methyl-2 : 4-dihydroxy acetophenone which was characterised by the formation of the phenylhydrazone and the oxime. Clemmensen reduction of this ketone led to 4 : 6-diethyl-5-methyl resorcinol.

5-Ethyl-6-methyl-2 : 4-dihydroxy-benzaldehyde, prepared from 4-ethyl-5-methyl-resorcinol, gave on reduction 4-ethyl-5 : 6-dimethyl resorcinol.

4-6-Diethyl-5-methyl-resorcinol, was converted into the aldehyde, 3 : 5-diethyl-4-methyl-2 : 6-dihydroxy-benzaldehyde, and this by Clemmensen reduction afforded 4 : 6-diethyl-2 : 5-dimethyl-resorcinol, a tetra-alkyl resorcinol.

The various alkyl resorcinols have been characterised by the formation of acetyl or *p*-nitrobenzoyl-derivatives, and those with a free position, *ortho* to the hydroxyl group, have been condensed with acetoacetic ester and malic acid by the Pechmann method to give coumarins.

### 90. A direct synthesis of 3-bromo-2-methoxybenzoic acid.

N. W. HIRWE and B. V. PATIL, Bombay.

Conditions have been investigated and the 3-bromo-2-methoxybenzoic acid has been successfully obtained by direct bromination.

### 91. Study of chloral-bromo-salicylamides.

N. W. HIRWE and B. V. PATIL, Bombay.

Chloral is condensed with the various bromo-salicylamides and its methyl ethers, such as (1) 3-bromo-salicylamide; (2) 5-bromo-salicylamide; (3) 3 : 5-dibromo-salicylamide; (4) 3-bromo-2-methoxy benzamide; (5) 5-bromo-2-methoxy benzamide; (6) 3 : 5-dibromo-2-methoxy-benzamide. Reactions of these condensation products with various reagents such, as (1) dimethylsulphate; (2) acetic anhydride; (3) benzoylchloride, etc. have been investigated.

### 92. Study of chloral-nitro-salicylamides.

N. W. HIRWE and MISS K. D. GAVANKAR, Bombay.

Chloral is condensed with various nitro-salicylamides and its methyl ethers, such as (1) 3-nitro-salicylamide; (2) 5-nitro-salicylamide; (3) 3 : 5-dinitro-salicylamide; (4) 3-nitro-2-methoxy-benzamide; (5) 5-nitro-2-methoxy-benzamide; (6) 3 : 5-dinitro-2-methoxy-benzamide. Reactions of these condensation products with various reagents such, as (i) dimethyl sulphate (ii) acetic anhydride; (iii) benzoyl chloride etc. have been investigated.



## 93. Interaction of sulphurylchloride with acid aryl amines.

D. R. SUKHATANKAR and G. V. JADHAV, Bombay.

Benzanilide is condensed with sulphuryl chloride in the presence of dry benzene, when benz-4-chloro-anilide is obtained. The work has been extended to benz-*o*, *m*, *p*-toluidides and benz-*p*-anisidide and chloro-derivatives obtained.

## 94. Derivatives of hydroxy-naphthoic acid.

S. N. RAO and G. V. JADHAV, Bombay.

In continuation of the work described before the acid chlorides of 4-chloro- and 4-bromo-acids have been prepared and various derivatives are made from them.

## 95. Experiments on the synthesis of paraberine. Part I. A synthesis of 8 : 17-diketo-6 : 17-dihydroparaberine.

S. N. CHAKRAVARTI and K. GANAPATHI, Chidambaram.

In order to throw some light on the reason why an angular structure like that of berberine is so commonly selected by nature and to test the validity of the suggestion that straight linear structures are more difficult to synthesise, the synthesis of paraberine was attempted. For this purpose  $\beta$ -naphthaquinone was first converted into isocoumarin-carboxylic acid, and the latter condensed with benzylamine. The benzylamine condensation product on treatment with aluminium chloride in nitrobenzene solution gave 8 : 17-diketo-6 : 17-dihydro-paraberine. All attempts to reduce the diketo compound to tetrahydroparaberine have so far been unsuccessful, but the problem is being further investigated.

In the second scheme, dibenzylketone was converted into its oxime, and the oxime reduced electrolytically to the amine. Attempts to convert the amine into compounds containing the four condensed rings of paraberine, by the action of formaldehyde or formic acid and subsequent treatment were unsuccessful, doubtless due to the absence of activating *p*-methoxy groups.

96. Chemical investigation of Indian medicinal plants. Part IV. Preliminary chemical examination of *Teramnus Labialis*.

S. N. CHAKRAVARTI and K. GANAPATHI, Chidambaram.

A systematic analysis of the entire plant, which is used as a cure for consumption, fever, and disorders of wind, bile and blood, has been made. The active principle of the plant appear to be a glucosiden acid, and two substances, m.p. 83° and 129°. These latter substances have been isolated in pure state. During working up of large quantities of the plant material, it was found that the nature of the active principles collected in different seasons differed. The physiological and pharmacological action, as well as the constitution of the active principles isolated, are under investigation.

## 97. Experiments on the synthesis of peri-quinolineazol (N-N). Part I. Attempted synthesis of tetrahydropერიquinolineazol (N-N).

S. N. CHAKRAVARTI and K. GANAPATHI, Chidambaram.

Attempts were made to synthesise peri-quinolineazol (N-N) which contains a fused quinoline and pyrazole nuclei, as such a synthesis



has an intrinsic interest of its own, and as such a ring system was assumed to be present in cytosine by Eurins. For this purpose *N*-aminodihydrocarbostyryl was (i) condensed with formaldehyde, (ii) converted into its formyl derivative, but attempts to cyclise these products were unsuccessful. Next *N*-aminodihydro-carboxyryl was converted into the benzoyl derivative, m.p. 168-169°. The benzoyl derivative on treatment with phosphorus oxychloride gave a substance, m.p. 212°.

Further experiments are in progress.

Quinoline-8-carboxylic acid, a starting substance for one of the schemes for synthesis, has been obtained in excellent yields by the oxidation of 8-methoxyquinoline with chromium trioxide and sulphuric acid.

98. *o*-Aldehydocarboxylic acids. Part II. A synthesis of 4-methoxyphthalaldehydic acid and a new synthesis of opianic acid.

S. N. CHAKRAVARTI and M. SWAMINATHAN, Chidambaram.

By the application of the new method of synthesis of *o*-aldehydocarboxylic acids recently discovered by us, 4-methoxyphthalaldehydic acid and opianic acid have been synthesised.

5-Methoxyhomophthalic acid was oxidised in boiling xylene solution by means of selenium dioxide to 4-methoxyphthalonic acid. The aniline derivative of 4-methoxyphthalonic acid, m.p. 165°, was then transformed into anilino-4-methoxy-phthalaldehydic acid, m.p. 179-180°, and the latter hydrolysed to 4-methoxyphthalaldehydic acid, m.p. 141°. This acid gives an oxime and was reduced to 5-methoxyphthalide, m.p. 119°.

3 : 4-Dimethoxyhomophthalic acid which had previously been obtained as an oil by Haworth, Koepfli and Perkin was obtained in a crystalline state, m.p. 116, and oxidised to the corresponding phthalonic acid. The aniline derivative, m.p. 156°, was then converted into anilino-opianic acid, m.p. 187-188° and the latter hydrolysed to opianic acid, m.p. 150°.

99. A new synthesis of 3 : 11-dimethoxy-oxyprotoberberine and a synthesis of 2 : 3 : 11 : 12-tetramethoxy-oxyprotoberberine.

S. N. CHAKRAVARTI and M. SWAMINATHAN, Chidambaram.

With the object of confirming the constitution of 3 : 11-dimethoxy-tetrahydroprotoberberine, 3 : 11-dimethoxyprotoberberine was synthesised in the following manner:—*N*- $\beta$ -*m*-methoxyphenyl-ethyl-5-methoxyhomophthalimide, m.p. 133°, prepared from 5-methoxyhomophthalic acid and  $\beta$ -*m*-methoxyphenylethylamine, was converted by hydrolysis into the corresponding amic acid, m.p. 167°. When the methyl ester (m.p. 85°) of this acid was treated with phosphorus oxychloride it gave a substance, m.p. 143°, identical with 3 : 11-dimethoxy-oxyprotoberberine previously obtained by Chakravarti, Haworth and Perkin from 3 : 11-dimethoxy-tetrahydroprotoberberine.

The method employed in the synthesis of 2 : 3 : 11 : 12-tetramethoxy-oxyprotoberberine was similar to that outlined above. 5 : 6-dimethoxyhomophthalic acid condenses with  $\beta$ -veratrylethylamine to yield *N*- $\beta$ -veratrylethyl-5 : 6-dimethoxyhomophthalimide, m.p. 180° which on careful hydrolysis is converted into *N*- $\beta$ -veratrylethylhomophthalamic acid, m.p. 165°. The methyl ester of this is converted in good yield by the action of phosphorus oxychloride into a substance, m.p. 190-191°, with properties characteristic of a compound of the oxyberberine type. This substance was found to be identical with 2 : 3 : 11 : 12-tetramethoxy-oxyprotoberberine obtained from 2 : 3 : 11 : 12-tetramethoxy-tetrahydroprotoberberine, and hence the constitution of the latter is confirmed.



# 100. Formation and transformation of carbon ring compounds. Part II.

S. C. SEN-GUPTA, Calcutta.

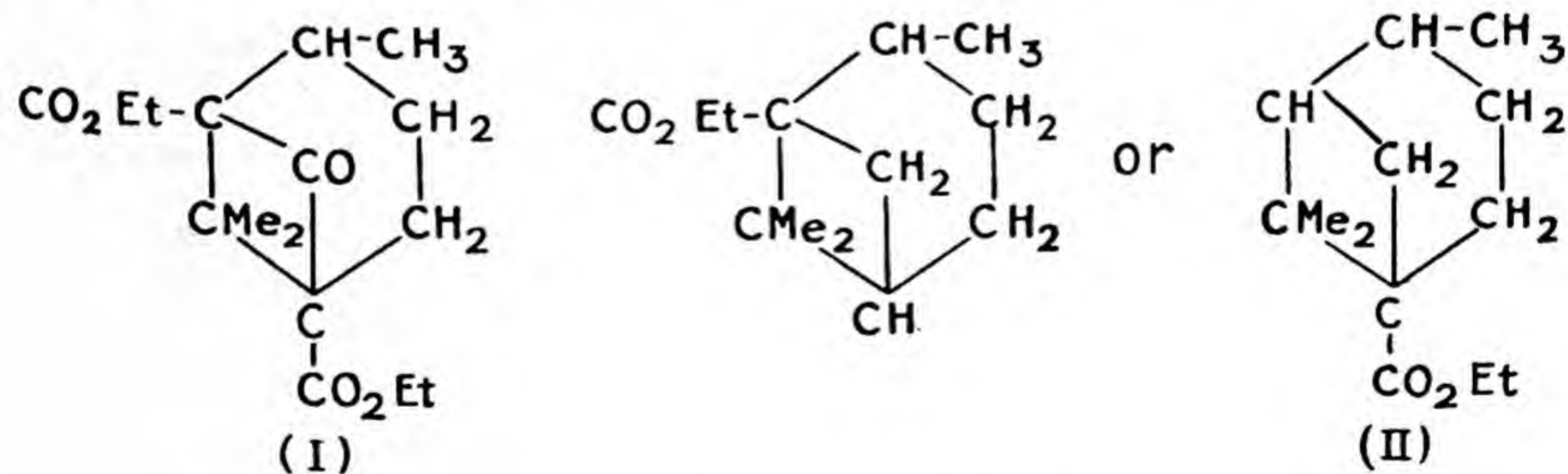
The anhydride of cyclopentane-carboxy-1-acetic acid condensed with toluene in presence of aluminium chloride giving cyclopentane-1-toluy-1-acetic acid (m.p.  $150^{\circ}$ ). This keto-acid on reduction by the clemmensen's method gave cyclopentane-1-(*p*-methyl)benzyl-1-acetic acid (m.p.  $69^{\circ}$ ), which on cyclisation with sulphuric acid gave 1-keto-1 : 2 : 3 : 4-tetrahydro-7-methylnaphthalene-3 : 3-spiro-cyclopentane (b.p.  $141-144^{\circ}/5$  mm.). Selenium dehydrogenation of this spiro-compound at  $300-350^{\circ}$  gave 3-methylphenanthrene instead of the expected 2-methylphenanthrene and  $\beta$ -methylantracene.

# 101. Studies in bridge formation, Part I. Syntheses of ketopinanedicarboxylic ester and pinane carboxylic ester.

R. C. DAS GUPTA and P. C. GUHA, Bangalore.

In continuation of the work described in last year's abstract on the syntheses of ethylketopopinane dicarboxylic ester (*Proc. Indian Sc. Cong.*, 1934, No. 113, p. 32), it has now been found that the disodium derivative of ethyl ketonorpinate reacts with  $\alpha$ -dibromobutane in a mixture of benzene and alcohol (3 : 7) and at high temperature to yield two products: (a) ethyl ketopinanedicarboxylate(I), b.p.  $118-120^{\circ}/12$  mm., and (b) bromoisobutyl-ketonorpinic ester, b.p.  $68-72^{\circ}/20$  mm., the latter only giving a pinkish coloration with ferric chloride.

Ethyl ketopinanedicarboxylate during reduction with zinc amalgam and concentrated hydrochloric acid suffers partial hydrolysis and decarboxylation (*cf. J.C.S.*, 1923, 123, 3145) and yields pinane carboxylic ester (II), b.p.  $150-152^{\circ}/27$  mm. Replacement of the carbethoxy group by hydrogen leading to the formation of pinane itself is being tried.



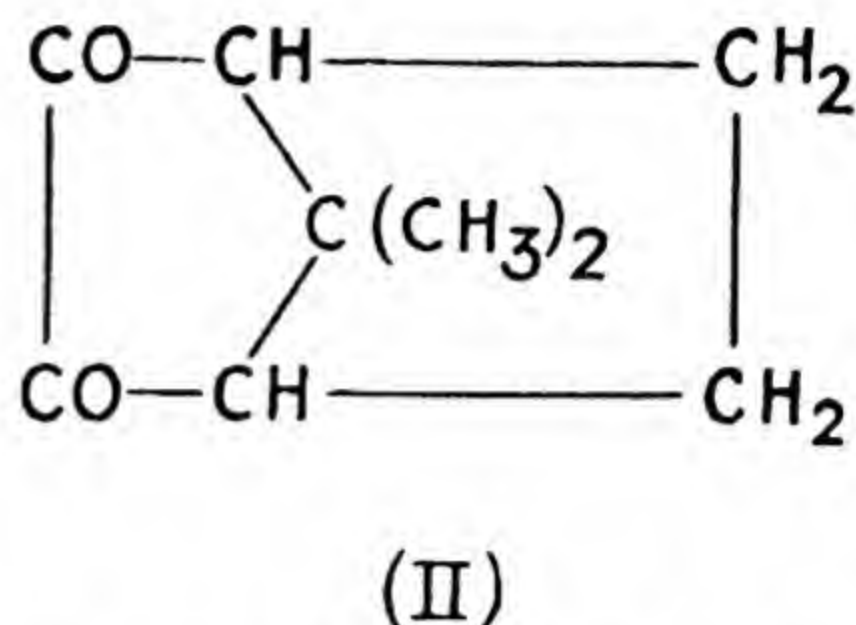
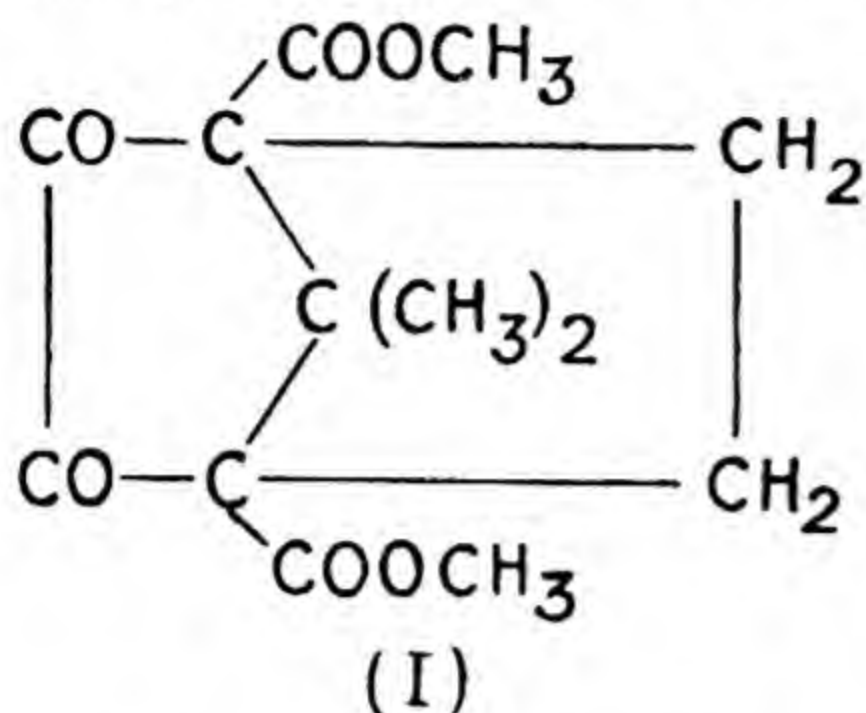
# 102. Studies in bridge formation. Part II. Attempts to synthesise bicyclic terpenes of the camphane group.

P. C. GUHA and S. K. RANGANATHAN, Bangalore.

The di-sodium derivative of dimethyl diketoapocamphorate was expected to give the bicyclic ester (I), on treatment with ethylene bromide.

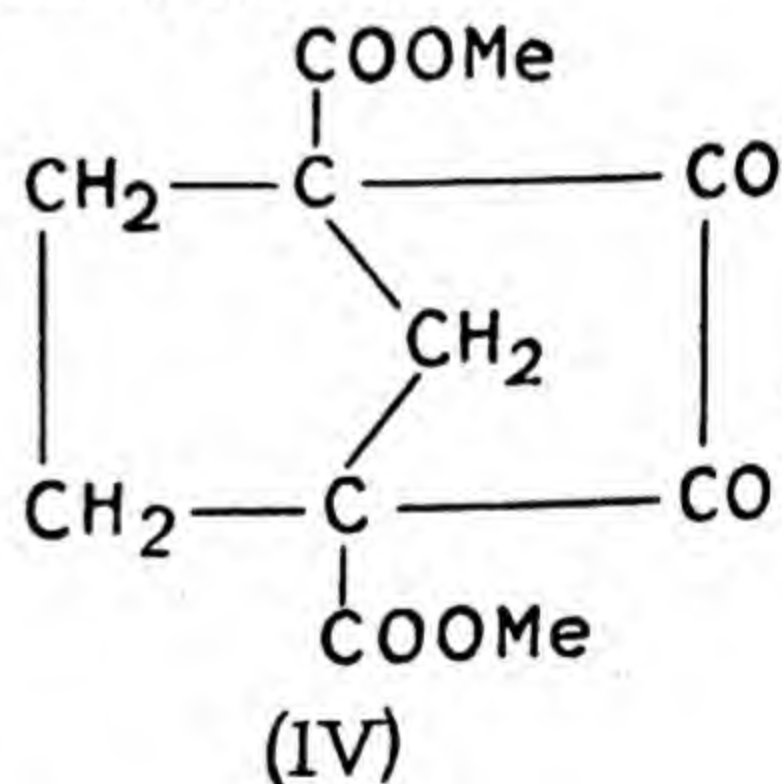
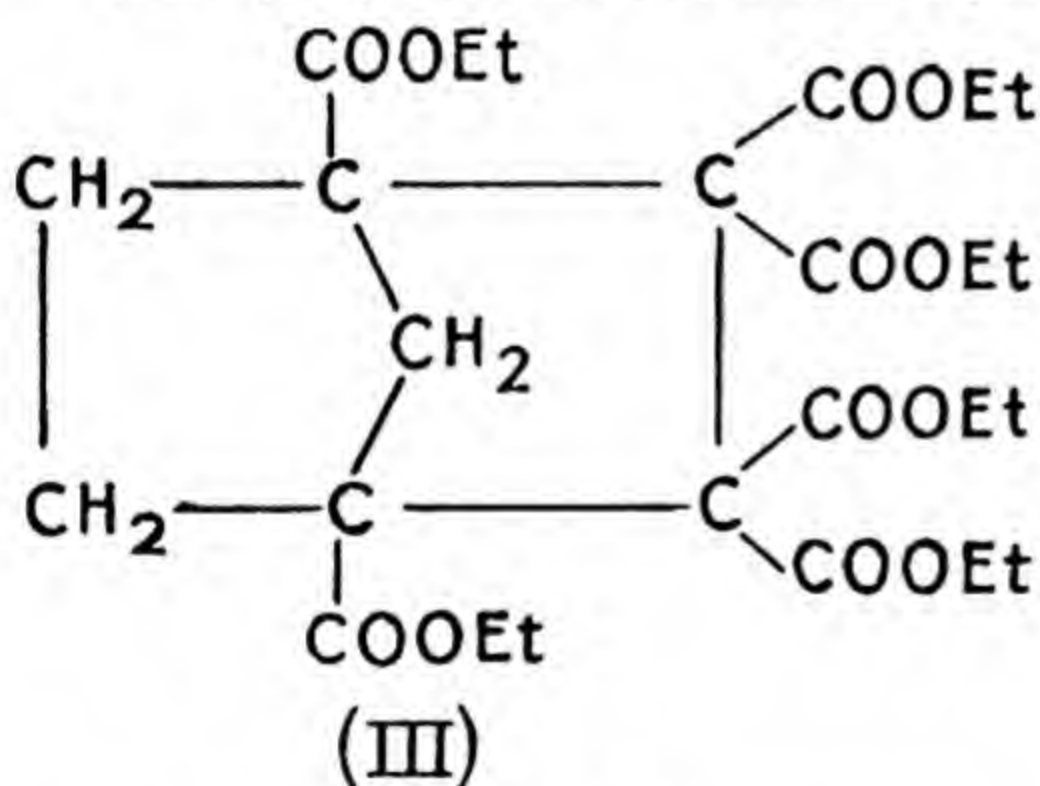


The ester (I), on hydrolysis and decarboxylation should yield *apocamphorquinone* (II), a substance as yet unknown.



The di-sodium compound of dimethyl diketo*apocamphorate* gave, on being heated in a sealed soda water bottle with ethylene bromide, in benzene or methyl alcoholic medium a beautiful crystalline ester, melting at 163.5-164.5°. Although, analytical values agreed with that of (I), no derivative of it has as yet been prepared. On hydrolysis, the ester gave a dicarboxylic acid, m.p. 274-275° (decomp.). The ester on being heated with dilute hydrochloric acid at about 170° gave a solid which was identified to be 1 : 1-dimethylcyclopentane-3 : 4-dione (*J.C.S.*, 1911, 99, 2012).

The (i) condensation of disodio-ethyl-ethane tetracarboxylate with ethyl  $\alpha\alpha'$ -dibromo-*cis*cyclopentane-1 : 3-dicarboxylate and (ii) a Dieckmann-Komppa reaction on methyl-*cis*-cyclopentane-1 : 3-dicarboxylate with methyl oxalate, have each yielded oily products which are being further studied. The former reaction is expected to give the bicyclic ester (III) and the latter the bicyclic diketonic ester (IV).



### 103. Studies in bridge formation. Part III.

K. N. GAIND and P. C. GUHA, Bangalore.

In an attempt to bridge methyl cyclohexane-2 : 3-dione-1 : 4-dicarboxylate (I) (*J. Indian Inst. Sci.*, 1932, 15A, 125) in which there are two hydrogen atoms replaceable by sodium and attached to the two *para* carbon atoms, with carbonyl bromide, two interesting products melting respectively at 210° and 145° have been obtained. The former is crystallised from alcohol-benzene mixture, while the latter from dilute alcohol. The molecular weight determination and combustion values of the former prove it to be compound (I) bridged by CO in position 1 and 4. The latter is being further studied. Bridging of (I) with chloracetol, methylene iodide, etc. is being tried.

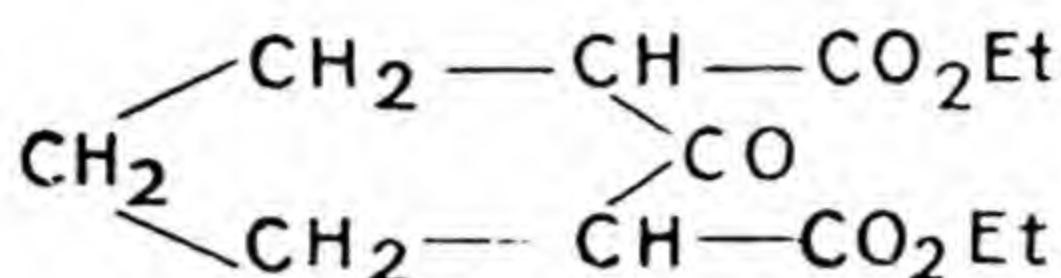


Hydrolysis and decarboxylation of compound (I) by heating with dilute hydrochloric acid under pressure at about  $120^{\circ}$  has yielded *cyclohexane-2 : 3-dione*, m.p.  $98.5^{\circ}$ .

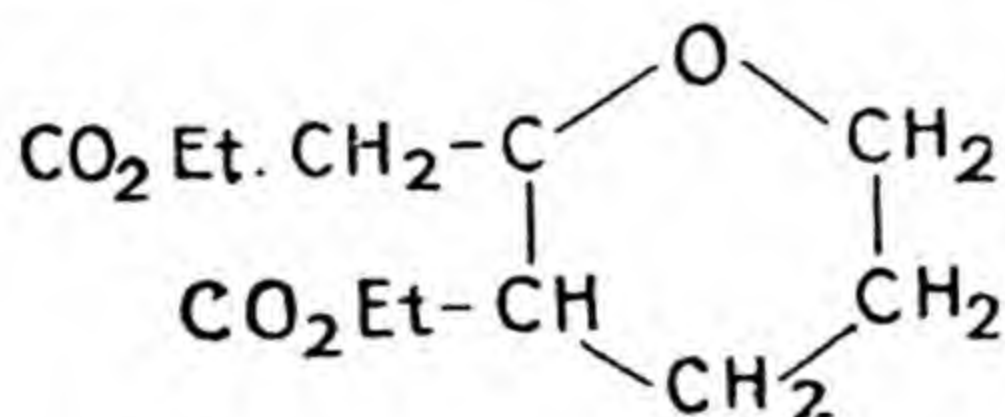
104. Studies in bridge formation. Part IV. Action of alkylene dibromides on acetone dicarboxylic ester.

P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

The sodium derivative of acetone dicarboxylic ester reacting with trimethylene bromide was expected to give a *cyclohexanone* derivative, having two replaceable hydrogen atoms in 2 : 6 positions.



The reaction was carried out in dry *benzene* suspension by heating under pressure for nearly 100 hours at  $140^{\circ}$ – $50^{\circ}$  in soda water bottles. From the petrol soluble portion of the reaction product (about half of the whole) on hydrolysis a di-basic acid was isolated, m.p.  $172^{\circ}$ , the corresponding mono-acid mono-ester had m.p.  $83^{\circ}$ . A similar reaction conducted by Perkin (*J.C.S.*, 1887, 51, 739) in absolute *alcohol* medium gave a product to which the following structure was given :



To this di-basic acid Perkin gives m.p.  $185$ – $92^{\circ}$  and to the corresponding mono acid mono-ester the m.p.  $115^{\circ}$ . These observations being obviously interesting, a thorough examination of the reaction products under the two sets of conditions (including our petrol insoluble portion) is being made.

105. Studies in bridge formation. Part V. Ring formation with carbonyl bromide.

P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

Mono-sodium derivative of malonic ester (2 mols.) reacts with trimethylene bromide, under modified conditions, to give a 50% yield of ethyl pentane-tetracarboxylate (1 : 1 : 5 : 5), Perkin's method giving only 15%. The disodium derivative of this reacts with carbonyl bromide to give *cyclohexanone-2 : 2 : 6 : 6-tetracarboxylic ester* (I) which on hydrolysis and decarboxylation by heating with 50% sulphuric acid for 16–20 hours over a free flame, gives *cyclohexanone*, identified through its typical derivatives. Alcoholic potash hydrolyses the tetra-ester to a tetra acid, m.p.  $246^{\circ}$ ; anilide m.p.  $315^{\circ}$ . Work is in progress for the conversion of the tetra-acid into the 2 : 6-dicarboxylic acid and the corresponding di-ester.



The disodium derivative of ethyl butanetetracarboxylate reacts similarly with carbonyl bromide to give ethyl *cyclopentanone*-2 : 2 : 5 : 5-tetracarboxylate, which on drastic hydrolysis and decarboxylation gives *cyclopentanone*, characterized through its semicarbazone.

106. Studies in bridge formation. Part VI. Attempts to synthesise bicyclic-terpenes of the thujane group.

P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

*cyclo*Hexanone-2 : 6-dicarboxylate, b.p. 140-2°/1.25 mm. prepared from ethyl pentane-1 : 1 : 5 : 5-tetracarboxylate according to the method of Ushakov (*J. Russ. Phy. Chem. Soc.*, 1929, 61, 795; cf. *Current Science*, 1934, 3, 20) forms in ethereal solution a di-sodium derivative which gives with bromine, under the separation of sodium bromide, an oily product b.p. 130-32°/1.25 mm. Its difference from the original *cyclohexanone* 2 : 6-dicarboxylic ester is proved from its boiling point and non-formation of sodium derivative. The bridged product gives with phenylhydrazine a derivative, m.p. 182°, as distinct from the corresponding derivative of the original *cyclohexanone* ester, m.p. 152-153°. Work is in progress for the conversion of the bridged *cyclohexanone* ester into the corresponding bridged hydrocarbon as also for the preparation of 3-methyl-*cyclohexanone*-2 : 6-dicarboxylate starting from methyl-trimethylene bromide and malonic ester.

107. Studies in bridge formation. Part VII. Attempts to synthesise bicyclic terpenes of the carane group.

P. C. GUHA and T. N. GHOSH, Bangalore.

By the action of bromine (2 atoms) on the disodium derivative of succinyldimalonic ester, ethyl *cyclohexan*-3 : 6-dione-1 : 1 : 2 : 2-tetracarboxylate has been obtained which, on hydrolysis by alcoholic potash in the cold, gives the corresponding tetra-acid in very poor yield. Work is in progress to convert the tetra-acid by decarboxylation into the dibasic acid, the ester of which, due to the presence of two reactive hydrogen atoms in 1 : 2-positions, will, it is expected, form the starting material for the synthesis of bicyclic terpenes of the carane group.

The reaction between the disodium derivative of succinyldimalonic ester and methylene iodide, carried out in toluene solution at 120-130°, yields a crude ester which, on hydrolysis by potash in the cold, yields in poor yield an acid in brilliant shining needles, m.p. 133-34°. Attempts are being made to improve the yield of the acid.

108. Studies in steric hindrance. Part VII. Nitration of brominated cinnamic acids and their esters.

P. RAMASWAMI AYYAR and J. D. VASAVADA, Bangalore.

Nitration of the following compounds has been studied under comparable conditions : (1) *cis*- and *trans*- $\alpha$ -bromo-cinnamic acids and their methyl esters ; (ii) *cis*- and *trans*- $\alpha$   $\beta$ -dibromo-cinnamic acids and their methyl esters ; and (iii)  $\alpha$   $\alpha$   $\beta$ -tri-bromo- $\beta$ -phenyl propionic acid and its methyl ester. The steric hindrance of the side-chain on position (2) of the nucleus in these compounds is found to increase progressively as shown by the fact that while about 35% *ortho*-nitration takes place in compounds of (i) above, no *ortho*-nitro-derivative could be isolated in the case of (ii) compounds ; while appreciable quantities of *meta*-nitro-derivative are formed in the case of (iii) compounds. The *para*-nitro-derivative is throughout the main by-product.



109. Studies in steric hindrance. Part VIII. Oxidative elimination of the carboxyl group in 3 and 4 nitro-phthalic acids with simultaneous replacement by a phenolic group.

P. RAMASWAMI AYYAR and J. D. VASAVADA, Bangalore.

Oxidation with acetone-permanganate of 3-nitro-phthalic acid yields a fair percentage of 3-nitro-salicylic acid (m.p.  $146^{\circ}$ ), while 4-nitro-phthalic acid gives a similar yield of 5-nitro-salicylic acid. The eliminated carboxyl group is either *ortho* or *para* to the nitro group, and an explanation for this is given on the polarity theory.

110. Studies in geometrical isomerism. Part III. The isomeric *cis* and *trans*  $\alpha$ -bromo-ortho-nitrocinnamic acids.

P. RAMASWAMI AYYAR and J. D. VASAVADA, Bangalore.

The *trans* compound (m.p.  $211-212^{\circ}$ ) is long known, but the *cis* isomer (m.p.  $159^{\circ}$ ) has now only been prepared by (i) nitration of *cis*- $\alpha$ -bromo-cinnamic acid; and (ii) the action of pyridin or alcoholic potash on *o*-nitro-cinnamic acid dibromide. From a chloroform solution containing traces of free bromine the *cis* isomer is quantitatively precipitated as the *trans*-compound (m.p.  $211-212^{\circ}$ ) by exposure to direct sunlight for a few minutes.

111. Studies in steric hindrance. Part V. The bromination of *o*-nitrotoluene.

P. RAMASWAMI AYYAR and D. R. MEHTA, Bangalore.

Using the following catalysts, iron, iron and iodine and antimony pentachloride in succession nearly 60% of 4-bromo-derivative and 40% of the 6-bromo-derivative of *o*-nitrotoluene are formed, whereas under comparable conditions chlorination yields 67% of the 6-chloro-derivative. This difference is attributed to the greater bulk of the bromine atoms and the consequent steric hindrance.

112. Studies in steric hindrance. Part VI. Condensation of *m*-nitrophenol with formaldehyde.

P. RAMASWAMI AYYAR and D. R. MEHTA, Bangalore.

The cyclic methylene ether  $C_8H_7O_4N$  (m.p.  $77^{\circ}$ ) of 2-hydroxy-6-nitro-benzyl alcohol (i.e. of 6-nitro-salicyl-alcohol) has been obtained in this reaction and this yields on oxidation 6-nitro-salicylic acid (m.p.  $167^{\circ}$ ).

113. Acid chlorides and thio-esters of 3-nitrophthalic acid.

G. C. CHAKRAVARTI and N. K. SESHADRIENGAR, Bangalore.

3-Nitrophthalic anhydride and phosphorus pentachloride were ground together and heated in an oil bath under reflux at  $140-145^{\circ}$  for 5 hours and then  $POCl_3$  removed under suction. The residue on being successively crystallised from  $CCl_4$  and petrol gave the acid chloride (I) m.p.  $77-78^{\circ}$ , yield 65%.

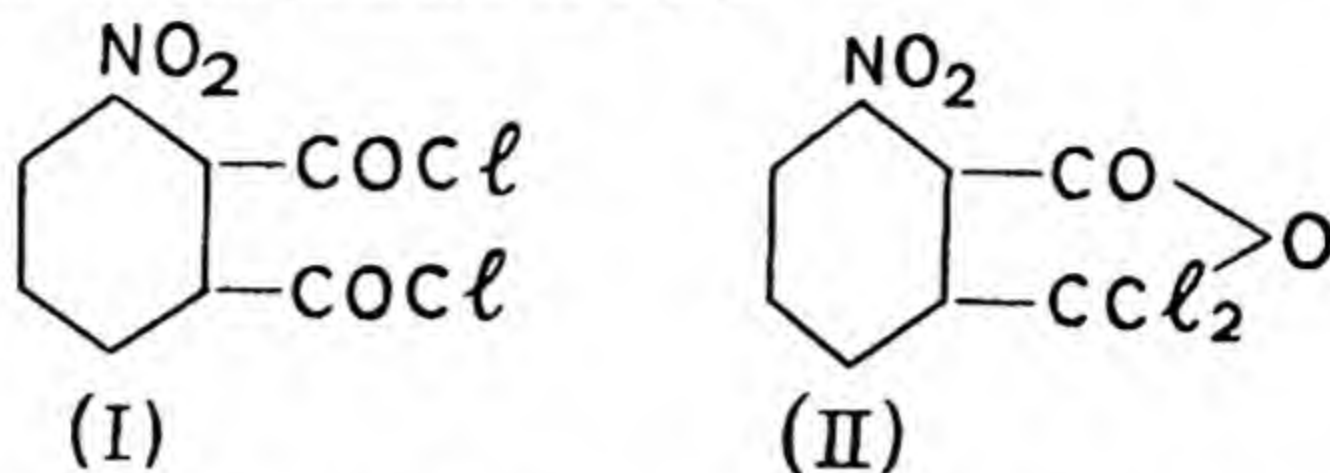
Asymmetrical form.—The other acid chloride (II) was prepared from (I) according to the method given in Organic Synthesis, Vol. XI, p. 88 and crystallised from petrol, m.p.  $124-25^{\circ}$ .

*p*-Tolyl-, phenyl-, benzyl-mercaptans were condensed with 3-nitrophthalyl chloride (I) in anhydrous benzene solution and in each case a product consisting of a solid and a thick viscous liquid were obtained, of



which the former ones on crystallisation from alcohol gave the following thio-esters : tolyl, m.p. 134-135°; phenyl, m.p. 105-106°; benzyl, m.p. 85°. The liquid fractions could not be purified by distillation as they decompose on heating.

The same thio-esters are formed from the mercaptans and 3-nitro-phthalic anhydride in presence of  $P_2O_5$ .



#### 114. Condensation of esters of $\beta$ -aryl-glutaconic acids with aromatic aldehydes.

G. R. GOGTE, Bangalore.

The  $\beta$ -aryl glutaconic acids contain a reactive methylene group. Consequently, the glutaconic esters from anisole, *o*-cresol-methyl ether, and *p*-cresol-methyl ether have been found to condense with benzaldehyde, anisaldehyde, etc. in presence of alcoholic potash to give the corresponding benzylidene glutaconic acids. The compound from anisole glutaconic acid and benzaldehyde melts at 213° (decomp.) and that with anisaldehyde at 164° (decomp.), while the compound from *o*-cresol-methyl ether glutaconic acid and benzaldehyde melts at 202° (decomp.) and that with anisaldehyde at 162° (decomp.).

#### 115. Geometrical isomerism in $\beta$ -aryl-glutaconic acids.

G. R. GOGTE, Bangalore.

The  $\beta$ -(2-methoxy-naphthyl-3-)-glutaconic acid has already been separated in its geometrically isomeric forms (*Proc. Indian Acad. Sci.*, 1934, 1, 57). It has now been observed that, on warming the *cis*-variety, m.p. 162° (decomp.), with dilute sodium hydroxide solution, an equilibrium mixture of the *cis* and *trans* forms is obtained, containing about 60 per cent. of the latter, m.p. 186° (decomp.). On the contrary, the *trans* variety is transformed into its *cis* isomer completely on being refluxed with strong solution of sodium hydroxide.  $\beta$ -(1-Methoxy-naphthyl-4-)-glutaconic acid, m.p. 199° (decomp.) (*ibid.*, p. 56) was similarly transformed into another form, m.p. 188° (decomp.), and the former has been proved to be the *cis*, and the latter to be the *trans* variety. The *cis*  $\beta$  (1-methyl-naphthyl-2-)-glutaconic acid, m.p. 161° (decomp.), prepared (*ibid.*, p. 54) was transformed into the *trans* variety, m.p. 152° (decomp.).

The glutaconic acids with the  $\beta$ -positions occupied by groups like anisole, *o*-cresol-methyl ether, *p*-cresol-methyl ether, etc. did not lend themselves to similar transformation. Thus the capacity of  $\beta$ -aryl glutaconic acids to exhibit geometrical isomerism seems to depend upon the volume of the radical occupying the  $\beta$ -position. Consequently glutaconic acids, where the  $\beta$ -position is occupied by heavy radicals, have been prepared from the coumaryl-4-acetic acids by hydrolysis and benzylation, and they have been shown to exist in two forms.

#### 116. Extension of Michael's reaction, Part VI.

T. N. GHOSH, Bangalore.

In part IV (Ghosh and Guha, *J. Indian Chem. Soc.*, 1934, 11, 355; cf. Indian Science Congress, Chemistry Abstracts, 1934, Nos. 127, 128)



it has been shown that a tricyclic compound is obtained by condensing ethyl  $\alpha\alpha'$ -phenylcarbonylacetone dicarboxylate (I) with an aldehyde ( $R\cdot CHO$ ). The work has been extended to study the effect of the group ( $R$ ) on the formation of the tricyclic ring. It is found that the tricyclic ring is obtained when  $R$  is phenyl, nitrophenyl,  $C_6H_4(OCH_3)$  or  $(Ph\cdot CH=CH)$ . If, however, the ester (I) is condensed, under exactly similar conditions, with formaldehyde or acetaldehyde, the *cyclobutane* ring is obtained. It is, therefore, evident that the formation of the tricyclic ring from the *cyclobutane* ring is conditioned by the atomic volume of the group ( $R$ ).

Ethyl acetonedicarboxylate reacts with  $\alpha$ -naphthyl-isocyanate to yield a piperidine compound, instead of the open-chain dinaphthylcarbonyl derivative analogous to compound (I). The piperidine derivative reacts with aldehydes to give bridged compounds.

### 117. Analysis of Indian coal tars and their distillation products.

B. J. HEGDE, B. SANJIVA RAO, and P. C. GUHA, Bangalore.

A fresh sample of thin coke over tar received from Jamshedpur (sp. gr. at  $15.5^\circ$ , 1.2171) gave the following percentage yields on distillation under standard conditions:— $110^\circ$ , 2.5;  $110-170^\circ$ , 0.3;  $170-270^\circ$ , 5.7;  $230-270^\circ$ , 7.6;  $270-350^\circ$ , 17.6; above  $350^\circ$ , 5.2; pitch 59.2. Evidently, the previous sample sent at our request was not a representative sample (*Proc. Ind. Sci. Cong.*, 1932, 19, 221).

### 118. Studies in bridge formation. Part VIII. Attempts to synthesise santene glycol.

B. H. IYER and P. C. GUHA, Bangalore.

The action of methylene bromide and *para*formaldehyde on diethyl-diacetyladiate was tried under various experimental conditions with the object of getting 1 : 3-diacetyl-*cyclopentane*-1 : 3-dicarboxylate. But due to the formation of resinous products from which no definite compound could be isolated, these methods had to be abandoned. The action of magnesium methyl iodide on the diacid chloride of *cyclopentane*-1 : 3-dicarboxylic acid is being studied and the expected diacetylpentane will be subjected to pinacone reduction.

### 119. Synthesis of some local anæsthetics.

K. N. GAIND, Bangalore.

Fourneau (*Bull. Soc. Chim.*, 1909, (iv) 5, 229-241) prepared benzoyl derivative of the methyl ester of dimethylamino-hydroxy-*isobutyric* acid and found it to be a very potent anæsthetic, quite feebly toxic, but very irritating to the tissues. With the hope of removing this irritating effect, attempts are being made to esterify the hydroxyl and carboxyl groups by different aromatic acids and alcohols. Three compounds, viz. the benzyl *o*- and *m*-tolyl esters have already been prepared.

Similar other compounds of higher aliphatic hydroxy acids, e.g.  $Me_2N\cdot CH_2\cdot CH_2\cdot CEt(OH)CO_2H$  are prepared and their efficiency as local anæsthetics studied.

### 120. Formation of heterocyclic compounds from dicarbethoxythioacetylcarbamic acid.

T. N. GHOSH, Bangalore.

Dicarbethoxythioacetylcarbamic acid (I) (*J. Indian Inst. Sci.*, 1933, 16A, 107) reacts readily with phenylhydrazine and hydrazine hydrate to give rise to 1 : 2 : 4-triazole and pyrazolone derivatives respectively.



With 4-substituted thiosemicarbazide, it yields a heptathiodiazine derivative in which there is a carbonyl-bridge in 1 : 4-position. The interaction of an aromatic amine with the compound (I) leads to the formation of a four-membered heterocyclic compound (with alternate carbon and nitrogen atoms) which in presence of alcoholic hydrazine hydrate is converted into a pyrimidine derivative. The rôle of hydrazine hydrate in bringing about this particular reaction is remarkable. With *o*-phenylenediamine, the compound (I) yields a benziminazole derivative.

Formation of the above compounds from dicarbethoxythio-acetyl-carbamic acid suggests that the latter can tautomerise to the thiol form by the wandering of either of the mobile hydrogen atoms attached to the adjacent nitrogen or to the carbon atoms.

## 121. Extension of Reformatsky's reaction. Part I. Action of ethyl bromomalonate on acetone.

B. H. IYER, Bangalore.

When ethyl bromomalonate reacts with acetone in presence of zinc, acetonylisopropyl-malonic ester  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH} \cdot (\text{CO}_2\text{Et})_2$  (b.p.,  $135-37^\circ/4$  mm.) is formed. The cyclic compound obtained from this ester on treatment with sodium ethylate, on hydrolysis with alkali, yields dimethyldihydroresorcin. The ester gives a semicarbazone, m.p.,  $72^\circ$ . Acid or alkaline hydrolysis gives a crystalline product (m.p.,  $133-34^\circ$ ) of the composition  $\text{C}_9\text{H}_{12}\text{O}_4$  and is supposed to be a lactonic acid; its constitution is under investigation.

## 122. Action of dihalogen compounds on oxalodiglycolic ester, Part I.

P. C. GUHA, Bangalore.

The sodium derivative of oxalodiglycolic ester does not react with ethylene bromide in alcoholic suspension even when heated to  $130-40^\circ$  for 60 hours; the reaction product on being worked up yielded only the unconverted ester.

When, however, the same reaction is conducted in benzene suspension the desired product, *viz.* 2 : 5-endoxy-2 : 5-dicarbethoxy-1 : 6-diketo-hexamethylene (m.p.  $165^\circ$ ) is obtained. This compound does not dissolve in alkali nor does it decolourise bromine water. On hydrolysis, the above dicyclic ester gives a compound agreeing in composition with the expected dicarboxylic acid. Work is in progress for obtaining the endoxy-diketo-hexamethylene from the above ester as also the condensation of other di-halogen compounds upon oxalodiglycolic ester.

## 123. Chemical examination of the roots of *Aristolochia Indica* (Linn), Part III. The essential oil.

U. S. KRISHNA RAO, B. L. MANJUNATH, and K. N. MENON, Bangalore.

On subjecting the essential oil for a systematic chemical examination and fractionation, it was found to consist mainly of sesquiterpinoid compounds : a hydrocarbon *Ishwarene*,  $\text{C}_{15}\text{H}_{24}$ , (b.p.,  $104-105^\circ/1$  mm.;

$$d_{30^\circ}^{30^\circ}, 0.9166; \eta_D^{30^\circ}, 1.5015; [\alpha]_D^{30^\circ}, -42.37^\circ;$$

hydrochloride : b.p.,  $128-130^\circ/1$  mm.), a ketone *Ishwarone*  $\text{C}_{15}\text{H}_{22}\text{O}$ , (b.p.,  $120^\circ/1$  mm.,

$$d_{30^\circ}^{30^\circ}, 1.0290; \eta_D^{30^\circ}, 1.5122; [\alpha]_D^{30^\circ}, -46.47^\circ;$$



semicarbazone : m.p.,  $240^{\circ}$  ; *p*-nitrophenyl hydrazone : m.p.,  $186.5$  ; 2 : 4 dinitrophenyl hydrazone : m.p.,  $167.5^{\circ}$ ), and an alcohol *Ishwarol*,  $C_{15}H_{24}O$  (b.p.,  $126-128^{\circ}/1$  mm. ;

$$d_{30^{\circ}}^{30^{\circ}}, 0.9926 ; \eta_{D}^{30^{\circ}}, 1.5098 ; [\alpha]_{D}^{30^{\circ}} \text{ in alcohol } -7.29^{\circ}.$$

In addition to these a small amount of camphor was also isolated.

It is interesting to note that when attempts were made to prepare the oxime of *Ishwarone*, an alkali insoluble derivative of the formula,  $C_{15}H_{23}ON$  (m.p.,  $136^{\circ}$ ), containing one active hydrogen atom was formed. This is probably an isoxime.

The structures of the new compounds isolated are being investigated.

#### 124. Chemical examination of the roots of *Aristolochia Indica* (Linn), Part IV. The bitter principles.

P. R. KRISHNASWAMY, B. L. MANJUNATH, and S. SIDDAPPA.  
Bangalore.

The isolation of two bitter principles from the roots of *Aristolochia indica* has already been reported. The present paper deals with a preliminary chemical study of them.

The first of these is a yellow, crystalline compound of the formula  $C_{17}H_{11}O_7N$ . This is insoluble in acids and possesses feeble acidic properties as evidenced by the formation of a monosodium salt. Its physical and chemical characteristics correspond to those of the substances of a similar nature, isolated by Pohl and others, and Hesse (*Arch. Pharm.*, 1895, 233, 284), and is isomeric with *aristolochic acid* (m.p.,  $215^{\circ}$ ). It has, therefore, been named *iso-aristolochic acid*.

A very careful examination showed that this was the only yellow bitter principle present in the roots. The paper contains some of the results of the chemical study of the compound.

The second substance is a colourless phenolic alkaloid, the isolation of which has already been reported (*Proc. Ind. Sci. Congress*, 1933, 210). When crystallised from toluene, it melted with decomposition at  $158.9$ . This material dissolved readily in methyl alcohol, but separated out soon ; it could then be crystallised only from a large volume of methyl alcohol, when it was obtained in the form of long needles melting sharply at  $215^{\circ}$ . The analytical results correspond to the formula  $C_{17}H_{19}O_3N$ , showing a close relationship with the bitter principle. So far, it has not been possible to prepare any crystalline derivatives, excepting the hydrochloride (m.p.,  $265^{\circ}$ ).

Further work is in progress.

#### 125. On the occurrence of acids with uneven number of carbon atoms in vegetable oils and fats.

U. S. KRISHNA RAO, B. L. MANJUNATH, and S. SIDDAPPA,  
Bangalore.

Gerard (*Compt. rend.*, 1880, 111, 305) was the first to claim to have isolated an acid with uneven number of carbon atoms, i.e. Daturic acid  $C_{17}H_{34}O_2$  from the oil of the seeds of *Datura Stramonium*. Since then a few acids of similar nature are said to have been obtained by various workers from different vegetable sources. A considerable amount of work questioning the above results is found recorded in the literature.

A systematic investigation of the oil from *Datura Stramonium* showed that the solid acids consisted only of palmitic and stearic acids with a small amount of lignoceric acid. No trace of daturic acid could be detected.



From the oil of *Butea Frondosa* Katti and Manjunath (*J. Indian Chem. Soc.*, 1929, 6, 839) isolated 2 fractions of acids corresponding to the formulae  $C_{23}H_{46}O_2$  and  $C_{25}H_{50}O_2$ . These could not be resolved by either chemical or physical means. Evidence is now presented to show that they are also eutectic mixtures of acids with even number of carbon atoms.

## 126. The structure of isopsoralen.

H. S. JOIS and B. L. MANJUNATH, Bangalore.

isoPsoralen  $C_{11}H_8O_3$  (m.p., 141-142°) obtained from the seeds of *Psoralea Corylifolia* (*Indian Science Congress*, 1934, Chemical Abstracts) is also found to belong to the class of coumarino-cumarones. The opening up of the coumarin ring and the formation of methoxyisopsoralic acid  $C_{12}H_{10}O_4$  (m.p., 142°) by methylation has already been reported.

The reduction of isopsoralen by sodium amalgam results in the formation of dihydro isopsoralic acid  $C_{11}H_{10}O_4$  (m.p., 124-125°) which lactonises only on heating to dihydroisopsoralen  $C_{11}H_8O_3$  (m.p., 74-75°). Both these compounds on oxidation with nitric acid give succinic acid. This definitely establishes the presence of the coumarin ring in the molecule, accounting for 2 of the oxygen atoms. The absence of a hydroxyl or methoxy group points to the rest of the molecule as consisting of a coumarone ring. Further proof of its structure as the result of oxidative degradations is offered.

The substance is in all probability identical or isomeric with angelicin isolated by Spâth and Pesta from the roots of *Angelica Archangelica* (*Ber.* 1934, 67, 853).

## 127. Studies on the preparation of starches from various grains and tubers.

H. P. DAS GUPTA, Bangalore.

*Rice Starch*.—Rice powder, which has been passed through 100 mesh sieve, is steeped in 0.5% caustic alkali for 48 hours and stirred at intervals. The whole suspension is then diluted until it attains a particular pH value and centrifuged. Two layers separate, the bottom one being about 97% pure (on moisture free basis), while the purity of the top layer is 92%. A number of cheap varieties of rice have been investigated as sources for the manufacture of rice starch.

*Juar Starch (Sorghum vulgare)*.—Juar is steeped in very dilute sulphurous acid and ground in the wet condition when it softens. It is then passed through a fine sieve and allowed to stand overnight. Two layers are easily separated, the bottom one being mostly starch. The layers are treated with different concentrations of dilute caustic alkali. A starch of about 95% purity is obtained.

*Ragi Starch (Eleusine coracana)*.—Although ragi contains a considerable amount of colouring matter which interferes with the preparation of starch, a clean white preparation can nevertheless be obtained by the method used. Ragi is ground wet and after passing through a fine sieve, allowed to stand overnight. The supernatant liquid is drained off and a dilute caustic alkali is used for the removal of protein and other undesirable materials. The starch obtained is approximately 96% pure.

*Sathi Starch (Curcuma zedoaria Roscoe)*.—*Curcuma zedoaria* grows wild in the low lying tracts of Bengal and in many parts of the west coast. The starch prepared out of it has a high viscosity comparable with that of potato starch and can usefully replace the latter which is now being imported in considerable quantities from abroad for use in the textile industry. The starch is prepared from the tubers by grinding the dried chips and passing through a fine sieve. This powder is steeped in



water and allowed to stand till it settles at the bottom. The supernatant liquid is syphoned off. The starch is separated by lixivation. The dried product is approximately 94% pure.

Investigation on the possibilities of other grains and tubers as sources of starch for use in different industries is in progress.

## 128. Influence of neutral salts on the enzymic hydrolysis of starch.

K. VENKATA GIRI and J. G. SHRIKHANDE, Bangalore.

The effect of neutral salts on the hydrolysis of starch by sweet potato amylase has been studied under varied conditions. The salts accelerate the action of the amylase on the acid side of the optimal pH 6.0 and were without any effect at the optimal pH, and at the alkaline side of the optimal pH at low concentrations. At high salt concentration there is retardation on the alkaline side of the optimal pH. The neutral salts accelerate the activity at pH below the optimum to an extent increasing with the acidity of the medium. The accelerating effect of the salts in relation to the concentration of the salt, enzyme and substrate has been investigated. The amylase preparations obtained by different methods—by (a) dialysis, (b) precipitation by alcohol, and (c) purification by adsorption on alumina gel displayed the same behaviour towards neutral salts. The anion is more concerned in the reaction than the kation. The accelerating effect is independent of the nature of the kation.

The apparently contradictory results obtained by several workers when studying the influence of neutral salts on the activity of vegetable amylases have been explained in the light of the foregoing observations.

## 129. A note on the Rideal-Stewart modification of Winkler's method for determining dissolved oxygen in waters.

R. H. RAMACHANDRA RAU, Bangalore.

The figures for dissolved oxygen in waters by the Rideal-Stewart modification were often lower than those by the Winkler method. This was ultimately traced to inadequacy of alkali in the alkaline iodide mixture prepared according to Thresh, Beale, and Suckling ('Examination of Waters and Water Supplies', 1933). As many of the commoner brands of caustic alkali are not quite pure, either the proportion of acid used for oxidation must be reduced or that of the alkaline iodide solution increased.

Work is in progress relating to (i) the conditions for absorption of oxygen by manganous hydroxide, and (ii) correction for reducing matter of the waters by direct reaction with potassium iodide and acid.

## 130. Examination of wax occurring in sandal leaves.

A. V. VARDARAJA IYENGAR, Bangalore.

It was found that hot alcohol extracts from sandal leaves waxy material which crystallises on cooling. A simple method of isolating it has been worked out. The wax which is yellowish white in colour consists of an acid, a primary alcohol, a secondary alcohol and a paraffin. Further studies on the chemical nature of the wax and relation of this to health and disease are in progress.

## 131. $\alpha$ -Clausenan and di- $\alpha$ -clausenan.

K. S. SUBRAMANIAN and B. SANJIVA RAO, Bangalore.

The Raman spectra of these compounds have been found and compared with those of some furane derivatives.



## 132. Santalol.

B. SANJIVA RAO, Bangalore.

The pure santalols have been found to be odourless. The odour has been found to be due to a comparatively volatile oxidation product of the santalols, which can be removed by repeated distillation.

## 133. Raman spectra of quinoline, quinaldine and isoquinoline.

S. K. K. JATKAR, Bangalore.

The following lines were observed :—

Quinoline : 389 (1), 457 (0), 516 (8), 604 (2), 755 (10), 980 (2), 1028 (5), 1162 (1), 1311 (2), 1368 (10), 1389 (3), 1428 (6), 1568 (6), and 3039 (5).

Quinaldine : 391 (3), 423 (3), 458 (4), 519 (8), 661 (0), 700 (1), 766 (10), 955 (0), 987 (0), 1011 (3), 1145 (0), 1205 (0), 1270 (1), 1312 (3), 1370 (10), 1423 (1), 1465 (2), 1556 (1), 1598 (1), 2923 (1), and 3047 (10).

isoQuinoline : 499 (10), 517 (10), 778 (10), 1008 (4), 1030 (5), 1132 (0), 1252 (1), 1278 (2), 1321 (5), 1378 (10), 1428 (5), 1457 (5), 1491 (0), 1551 (2), 1580 (3b), 2448 (0), 2490 (1), and 3047 (8).

The striking similarity of the spectra to those of benzene, pyridine, picolene and naphthalene is discussed.

134. Raman spectra of *cis* and *trans* cyclohexanes and dekalins.

S. K. K. JATKAR, Bangalore.

According to Sachse-Mohr strainless multiplaner ring structure cyclohexane should exist as a chair or cradle form. This hypothesis lacks experimental support. Although it has recently been shown that the transform is the only stable form Huckel has pointed out the small energy difference between the coplaner and multiplaner models as the cause of difficulty in distinguishing among the possible derivatives of the isomers.

Attempt has been made to find evidence for the existence of the two possible forms by studying the Raman effect of pure cyclohexane, (m.p.  $6.4^{\circ}$ ) and the same treated with aluminium chloride as suggested by Zelinski (m.p.  $-43^{\circ}$ ). The difference between the two spectra is the complete disappearance of the line  $400\text{-}1\text{ cm.}$  in cyclohexane treated with  $\text{AlCl}_3$  the other shifts remaining sensibly the same. Search was also made for lines due to possible decomposition products. A similar study of the *cis* and *trans* dekalins did not show appreciable difference between the two spectra.

## 135. The study of antimony electrode.

D. N. MEHTA and S. K. K. JATKAR, Bangalore.

Using the apparatus described in the *Proc. Indian Science Congress*, 1934, Bombay, the electrode potentials of antimony electrodes with solutions of various pH values have been determined. The value of the potential  $\text{Sb/Sb}_x\text{O}_y$  deduced from this has been confirmed by direct measurement against a hydrogen electrode and the temperature coefficient of the system has been determined. The results indicate that the stick antimony electrode whether freshly polished or allowed to tarnish shows a potential corresponding to the formation of antimony tetroxide. The system  $\text{Sb/Sb}_2\text{O}$  is another possibility of the electrode reaction, which is further supported from the results obtained from experiments carried out on similar lines with bismuth electrodes.



136. Raman spectra of  $\beta$ -pinene and dipentene.

R. PADMANABHAN and S. K. K. JATKAR, Bangalore.

Previous work of the Raman spectrum of  $\beta$ -pinene is confined to the region  $\lambda 4358$ – $\lambda 4916$  and there seems to be no data on dipentene at all. In our work we have not only recorded the shifts due to  $\lambda 4046$  but also additional frequencies due to the 4358 line. The Raman spectrum of dipentene surprisingly enough seems to have very little resemblance to that of limonene. Since the identification of limonene and dipentene in a mixture is very difficult on account of their close resemblance in physical and chemical properties, this difference in light scattering appears, therefore, to have some practical use in detecting one in presence of the other.

137. The anomalous rotatory dispersion of  $\beta$ -pinene. Part I.

R. PADMANABHAN and S. K. K. JATKAR, Bangalore.

This paper discusses the various possibilities by which one could explain the anomalous rotatory dispersion of  $\beta$ -pinene. (1) It is not due to Cotton effect because there is no evidence of any absorption in the region of the anomaly. (2) In our previous work sabinene had also been found to be anomalous (*Indian Science Congress*, Abstracts, 1932) and since this compound resembles  $\beta$ -pinene in having a semicyclic double bond adjacent to an asymmetric carbon atom it was considered that the anomaly might be due to the superposition of an opposite rotation due to the induced asymmetry of the semicyclic double bond. The absence of any anomaly in camphene, however, shows this hypothesis to be untenable. (3) On prolonged purification by fractional distillation, it is found that there is a gradual transition from a laevorotating substance in the first fractions to a dextrorotatory substance of higher rotatory dispersive power in the tail fractions. The explanation of the anomalous rotatory dispersion would thus appear to lie in the heterogeneous character of the substance. An analysis of the Darmoni diagram reveals a three component system. The anomaly seems to be an inherent characteristic of the  $\beta$ -pinene molecule.

## 138. Continuous hydrogenation of vegetable oils.

J. G. KANE, Bangalore.

Vegetable oils such as groundnut and cocoanut oils have been hydrogenated with a new nickel catalyst that has been found to be very active and resistant to poisons. The catalyst has been used in a form suitable for continuous operation in plants of varying sizes specially manufactured for the purpose. Thus experiments have been carried out in a glass model on a laboratory scale and on a semi-commercial scale in an all-metal plant fitted up with all the appliances. With the latter plant, the yield of hardened product, m.p.  $35^{\circ}$  to  $40^{\circ}$  (from groundnut oil), was 3 lbs. per hour per lb. of nickel, under optimum conditions.

Experiments conducted under varying pressures—20 to 80 lbs. per sq. inch—and temperatures between  $120^{\circ}$  and  $180^{\circ}$  show that the above continuous process can be worked economically under a pressure of 60 lbs. per sq. inch and at a temperature range of  $120^{\circ}$  to  $130^{\circ}$ .

## 139. Effect of addition of reagents on the pH of rotary drilling fluids.

D. N. MEHTA, Bangalore.

pH values of tannins from myrobolan powder have been determined by employing bismuth, quinhydrone and antimony electrodes. The



effect of addition of sodium hydroxide, hydrochloric acid and tannins (from myrobolan powder) on the pH values of the rotary drilling fluids has been studied hydrogen electrode being used, thereby rationalizing the procedure governing the adsorption of added reagents by rotary drilling fluids.

#### 140. The constitution of vasicin.

K. S. NARANG and J. N. RAY, Lahore.

The Spath structure for peganin is criticised and synthetical experiments are described in support of the structure advocated by Narang and Ray.

#### 141. Synthesis of coumarins and chromones.

D. CHAKRAVARTI, Calcutta.

The condensation of various mono-, di- and tri-hydric phenols with  $\beta$ -ketonic esters shew conclusively that Simonis' reaction is not of general applicability (Chakravarti, *J. Indian Chem. Soc.*, 1931, 8, 129, 407, 619; 1932, 9, 25, 31, 389). It has been observed throughout this investigation that coumarins are always produced using sulphuric acid but phosphorus pentoxide may produce either coumarins or chromones. Excepting in the case of condensation of  $\alpha$ -naphthol with unsubstituted acetoacetic ester no other case has been detected where a chromone is formed even in traces using sulphuric acid (*cf.* Dey and Lakshminarayanan, *J. Indian Chem. Soc.*, 1932, 9, 149). Attention was, therefore, directed towards the investigation of the part played by phosphorus pentoxide in the formation of chromones as well as towards the possibility of substituting any other condensing agent for phosphorus pentoxide. Thus various acidic, basic and neutral condensing agents, e.g. phosphoric acid, zinc chloride, hydrochloric acid gas, sodium ethoxide, boric anhydride, sodium acetate have been tried. It is remarkable to note that if condensation takes place then coumarins are always formed in these cases and all attempts to find a substitute for phosphorus pentoxide have failed.

It may also be noted that sulphuric acid in Pechmann's reaction may with advantage be replaced by phosphoric acid particularly in the case of polyhydric phenols, when better yields and purer products are obtained. It has also been found by the author that in Bülow's reaction, which is similar to Pechmann's reaction, the condensation of phenols with  $\beta$ -diketones may also be effected with advantage using sulphuric acid or better phosphoric acid.

#### 142. Constitution of chloro-resorcinol, chloro-resorcyaldehyde and nitro-resorcyaldehyde.

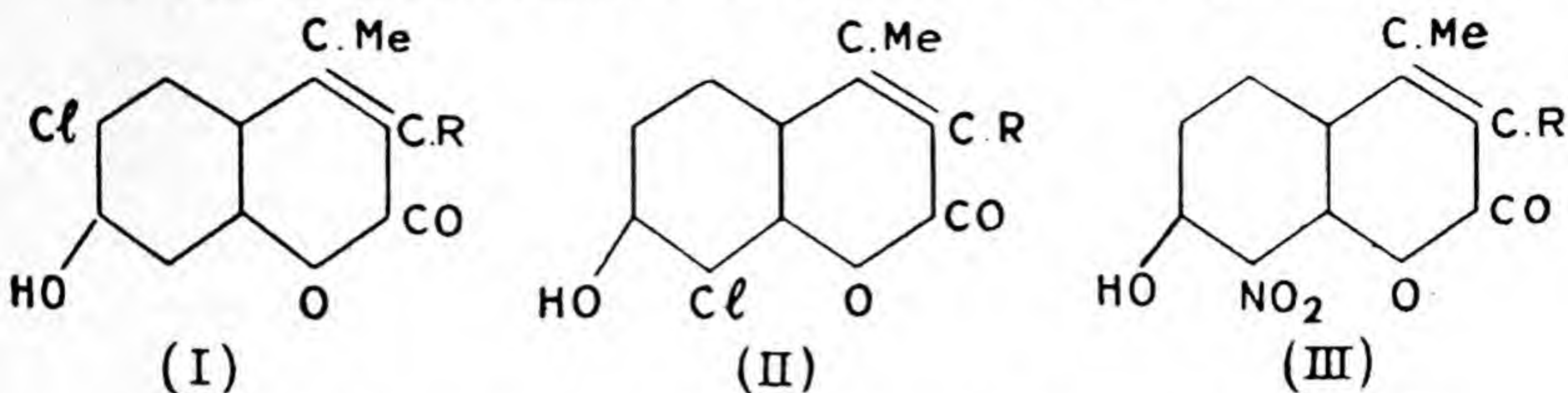
D. CHAKRAVARTI and B. N. GHOSH, Calcutta.

The condensations of halogenated and negatively substituted polyhydric phenols with  $\beta$ -ketonic esters forming substituted coumarins have furnished a ready means for determining the constitution of the substituted phenols and their derivatives.

(2 or 4)-Chloro-resorcinol, prepared according to the method of Reinhard (*J. pr. Chem.*, 1878, 17, ii, 336), condenses with acetoacetic ester and its C-methyl derivative to form 6 or 8-chloro-coumarins (I or II). The nitration of  $\beta$ -methyl-umbelliferone (*cf.* Pechmann and Cohen,



Ber., 1901, 34, 666) and 3 : 4-dimethyl-umbelliferone gives 8-nitro derivatives (III) as they are identical with the condensation products of 2-nitro-



resorcin with acetoacetic ester and its C-methyl-derivative respectively. These 8-nitro-coumarins, on reduction give 8-amino-coumarins, which form stable diazo-anhydrides. The diazo-anhydrides, on treatment with cuprous chloride in hydrochloric acid, give 8-chloro-coumarins which are different from the condensation products of chloro-resorcinol with the acetoacetic esters, which must therefore, be 6-chloro-coumarins (I). Chloro-resorcinol is, therefore, 4-chloro-resorcinol. A direct synthesis of 6-chloro-coumarins from 6-nitro-coumarins (the condensation products of 4-nitro-resorcin with the acetoacetic esters) is being attempted.

Chloro-resorcinol and 2-nitro-resorcin condense with malic acid to give good yields of coumarins, and it is expected that the formation of coumarins from chloro-resorcyraldehyde and nitro-resorcyraldehyde (Gattermann, *Annalen*, 1907, 357, 313) by their condensation with malonic acid would also settle the position of the substituents in chloro- and nitro-resorcyraldehydes.

#### 143. Synthesis of coumarins from phenols and $\beta$ -ketonic esters using phosphorus pentoxide. Part III. Coumarins from chloro-resorcinol.

D. CHAKRAVARTI and B. N. GHOSH, Calcutta.

It has so long been supposed that the presence of a halogen atom in the phenolic nucleus greatly hinders Pechmann's reaction in the synthesis of coumarins and the presence of a negative substituent like  $\text{NO}_2$  or  $\text{COOH}$  totally inhibits the reaction (Clayton, *J. Chem. Soc.*, 1908, 93, 2018). It has been found by the authors that even if there be a halogen atom or a negative substituent in resorcinol, which has the faculty of the formation of coumarins with great readiness in Pechmann's reaction, the reaction takes place smoothly forming substituted coumarins. Thus 2-nitro-resorcin condenses with acetoacetic ester and its C-methyl derivative to form coumarins in good yield.

Chloro-resorcin, prepared according to the method of Reinhard (*J. pr. Chem.*, 1878, 17, ii, 336) has been condensed with acetoacetic ester, C-methyl-, C-ethyl-, C-propyl-, C-isobutyl-, C-benzoyl, and  $\alpha$ -chloro-acetoacetic esters, acetone dicarboxylic ester, benzoyl acetic ester and aceto-succinic ester in presence of sulphuric acid to give good yields of coumarins. By changing the condensing agent for phosphorus pentoxide in some of these condensations identical coumarins are obtained as is proved by their mixed melting points and also by the identity of their derivatives as was previously observed by one of us (Chakravarti, *J. Indian Chem. Soc.*, 1931, 8, 129, 407).

Condensations of bromo-resorcinol, iodo-resorcinol, resorcylic acid and the negatively substituted orcinol, pyrogallol, *m*-cresol, *p*-cresol, and the naphthols with  $\beta$ -ketonic esters are in progress.



144. Studies in the *iso*-flavone series.

P. C. MITTER and S. MAITRA, Calcutta.

On condensation with hippuric acid, 2 : 4-dimethoxy- $\beta$ -resorcyaldehyde gives an azlactone, m.p. 168°, which on hydrolysis gives 2 : 4-dimethoxy-phenylpyruvic acid, m.p. 155°-156°. The oxime of the acid, m.p. 145° was converted by the usual method into 2 : 4-dimethoxy-phenylacetone, m.p. 75°. On condensation with phloroglucin by Hoesch's method, the nitrile gave phlor-2':4'-dimethoxy-phenylacetophenone, m.p. 175°.

It is proposed to condense the ketone with formic ester and to demethylate the product to 2':4':5:7-tetraoxy-*isoflavone*.

## 145. Studies in the anthraquinone series.

P. C. MITTER and P. DUTTA, Calcutta.

3-Nitrophthalicanhydride condenses with phenol in presence of  $\text{AlCl}_3$ , the only product of the reaction being 3-nitro-2-(2-hydroxybenzoyl)-benzoic acid, m.p. 238°. On reduction it gives 3-amino-2-(2-hydroxybenzoyl)-benzoic acid, m.p. 217°, which on diazotisation gives 3-hydroxy-2-(2-hydroxybenzoyl)-benzoic acid, m.p. 199°-200°. On ring-closing with fuming sulphuric acid and boric acid, chrysazine is obtained.

3-Nitrophthalic anhydride condenses with anisole at 0° in presence of aluminium chloride. Two products are formed which are separated by fractional crystallisation from methyl alcohol. The main product of the reaction which crystallises from dilute methyl alcohol is 3-nitro-2-(4-methoxybenzoyl)-benzoic acid, m.p. 208°. This gives on reduction 3-amino-2-(4-methoxybenzoyl)-benzoic acid, m.p. 169°-71°, which on diazotisation gives 3-hydroxy-2-(4-methoxybenzoyl)-benzoic acid, m.p. 202°. On ring closure with fuming sulphuric acid and boric acid and subsequent demethylation 1 : 6-dihydroxyanthraquinone, m.p. 270°-72°, is obtained.

The other product of the reaction, which crystallises from methyl alcohol, is most probably 6-nitro-2-(4-methoxybenzoyl)-benzoic acid, m.p. 214°.

146. The chemical examination of the seeds of *Nyctanthes arborescens*.

P. S. VARMA and S. K. SHARMA, Benares.

The preliminary examination of the seeds has been carried out and a bitter principle, resin, 2.5% fixed oil, a small percentage of essential oil, sterol, tannins, phlobaphenes, water soluble gums, etc. have been isolated. Work with larger amounts of the material is in progress.

147. Halogenation. Part XIII. Bromination and iodination of *o*-, *m*-, and *p*-xylenes.

P. S. VARMA and K. S. VENKATARAMAN, Benares.

Mono-iodo-xylenes have been obtained before in fairly good yields by the methods worked out in this laboratory (Varma and Kulkarni, *J. Indian Chem. Soc.*, 1926, 3, 291; Varma and Panickar, *ibid.*, 342). Only one di-iodo-*m*-xylene has been obtained before and that by a tedious process (Hammerich, *Ber.*, 1890, 23, 1635; Tohal, Bauch, *Ber.*, 1893, 26, 1105). The authors have succeeded in preparing di-iodo-*o*-xylene and di-iodo-*p*-xylene for the first time in good yields and 4-iodo-6-nitro-*m*-xylene, 2-iodo-5-nitro-*p*-xylene by direct methods.

Bromination of the three xylenes has been more exhaustively studied in (1) sunlight, (2) in sunlight in presence of halogen carriers, and (3) in the dark in presence of halogen carriers. From the results obtained



it is clear that in sunlight substitution in side-chain alone occurs whereas with the combined effect of sunlight and the other halogen carriers substitution in both the side-chain as well as in the nucleus takes place. In the dark when only nuclear substitution takes place, the yield of the nuclear products is considerably increased in presence of halogen carriers.

148. Halogenation. Part XIV. Preparation of the mixed halogen derivatives of xylenes.

P. S. VARMA and K. S. VENKATARAMAN, Benares.

A study of the literature shows that the majority of the mixed halogen compounds of xylenes have been obtained by indirect methods from diamino-compounds by successive replacement of the amino groups by halogens through the Sandmeyer's reaction. A number of mixed halogen compounds, such as 4-chloro-6-bromo-*m*-xylene, 2-chloro-5-bromo-*p*-xylene, 4-bromo-5-iodo-*o*-xylene, 4-bromo-6-iodo-*m*-xylene, 2-bromo-5-iodo-*p*-xylene, 4-chloro-6 (?) -iodo-*p*-xylene, 2-chloro-5 (?) -iodo-*p*-xylene have been obtained by direct halogenation and some of these compounds, especially the iodo-derivatives have been obtained for the first time.

149. Halogenation. Part XV. Halogenation of *p*-cymene, propyl-benzene and cumene.

P. S. VARMA and M. K. SRINIVASAN, Benares.

*p*-Cymene has been chlorinated in diffused day-light in presence of halogen carriers as a result of which mono-chloro- and di-chloro-*p*-cymenes have been obtained in varying yields. In the dark, however, only mono-chloro-*p*-cymene has been obtained in varying yields. In sunlight both nuclear and side-chain substituted chloro-derivatives have been obtained. By the direct bromination of 2-chloro-*p*-cymene, 2-chloro-5-bromo-*p*-cymene has been obtained.

When propyl-benzene and bromo-propyl-benzene are directly iodinated in presence of some substances, mono-iodo-, and di-iodo-propyl-benzene and bromo-iodo-propyl-benzene are obtained.

By the study of chlorination and iodination of cumene under different conditions it has been possible to find out the best conditions under which *p*-chloro-cumene, dichloro-cumene, *p*-bromo-cumene, dibromo-cumene, cumene mono-bromide, cumene dibromide, cumene monochloride and cumene dichloride are obtained.

150. Halogenation. Part XVI. Bromination and iodination of mesitylene and pseudo-cumene.

P. S. VARMA and T. S. SUBRAMANIAN, Benares.

Bromination and iodination of mesitylene and iodination of pseudo-cumene have been more exhaustively studied under different conditions in presence of a number of substances and the conditions for getting the best yield of the halogen derivatives determined.

151. Halogenation. Part XVII. Bromination and iodination of diphenyl and benzidine.

P. S. VARMA and M. KRISHNAMURTHI, Benares.

By the direct bromination and iodination of diphenyl, dibromo- and di-iodo-diphenyl have been obtained in good yields. By indirect methods also these bromo- and iodo-compounds have been prepared from benzidine.



152. A new method of preparing organo-mercuric compounds of phenols and aromatic amines. Part II.

PANCHANAN NEOGY and G. K. MUKHERJI, Calcutta.

The work of Neogy and Chatterji (*J. Indian Chem. Soc.*, 1928, 221) has been continued and organo-mercuric compounds of many phenols, nitro-phenols, amines, and nitro-amines have been prepared by the same method with suitable modifications. In this manner  $\alpha$ -,  $\beta$ -naphthols, thymol, carvacrol, *o*- and *p*-nitro-phenols as also  $\alpha$ -,  $\beta$ -naphthylamines, toluidines, xylidines, anisidine, benzidine, and *o*- and *p*-nitro-anilines have been mercurated.

153. A new method of preparing organo-mercuric compounds of phenols and aromatic amines. Part III.

PANCHANAN NEOGY and G. K. MUKHERJI, Calcutta.

An interesting observation has been made in the course of the present work that *N*-mercury compounds can be converted to the *C*-mercury compounds by dissolving them in dilute hydrochloric acid and subsequently reprecipitating with sodium bicarbonate whereby the mercury atom travels from the nitrogen atom to the nucleus. In this manner *C*-mercury compounds of aniline, toluidines, xylidines,  $\alpha$ -,  $\beta$ -naphthylamines, anisidine, and benzidine have been prepared.

154. Resolution of co-ordinated inorganic compounds into optical isomers. Part III—Tri-propylenediamine compounds of cadmium.

PANCHANAN NEOGY and G. K. MUKHERJI,  
Calcutta.

Co-ordinated compounds of cadmium containing three molecules of ethylene diamine (Neogy and Mukherji, *J. Indian Chem. Soc.*, 1934, 225) and of zinc (Neogy and Mukherji, contributed to *J. Indian Chem. Soc.*) have been resolved. Attempts to prepare tri-propylene diamine compounds of cadmium have been successful and these are being resolved. Work on this subject is in progress.

155. Chemical examination of the seeds of *Hygrophyla Spinosa*.

N. L. PHALNÍKAR, K. S. NARGUND, and D. D. KANGA,  
Ahmedabad.

The drug belongs to the N.O. Acanthaceæ and is used in jaundice, anasarca and dropsy; it is also used as a tonic. The powdered seeds were successively extracted with various solvents. The results are indicated in the following table:—

Solvent.	Extract.	Nature of the extract.
1. Petroleum ether (b.p. 40° to 60°).	21%	A pale yellow mobile transparent oil with aromatic odour.
2. Ether ..	1.06%	A dark-red opaque semi-solid mass.
3. Chloroform ..	0.5%	A dark-red liquid.
4. Alcohol ..	8.87%	Thick resinous mass.



The moisture present in the seeds was found to be 8.43%. The seeds were found to contain both sugar and an enzyme. The following are the constants of the oil from the petroleum ether extract :—

Density at 30°	..	0.9254
N <sub>D</sub> 33°	..	1.469674
Iodine value	..	122.1
Saponification value	..	206.5
Acid value	..	2.65
Unsaponifiable matter	..	7.52%
R.M. value	..	0.252
Polenske value	..	0.461

Further work is in progress.

#### 156. Chemical examination of the seeds of *Clitoria ternatea*.

J. D. RAWAL, K. S. NARGUND, and D. D. KANGA, Ahmedabad.

The drug belongs to the N.O. Leguminosæ and is used as a mild purgative and a diuretic.

The powdered seeds were successively extracted with various solvents. The results are indicated in the following table :—

Solvents.	Extract.	Nature of the extract.
1. Petroleum ether (b.p. 40° to 60°).	8.17%	Greenish mobile liquid with bitter smell and taste.
2. Ether	1.54%	Dark-red thick liquid.
3. Chloroform	1.94%	Greenish thick liquid.
4. Alcohol	6.53%	Dark reddish resinous liquid.

The moisture present in the seeds was found to be 6.4%. The following are the constants from the petroleum ether extra ct.

Density at 30°	..	0.90015
N <sub>D</sub> 33°	..	1.46809
Iodine value	..	80.31
Saponification value	..	205.65
Acid value	..	2.82
Unsaponifiable matter	..	6.906%
R.M. value	..	0.1850
Polenske value	..	0.3701

Further work is in progress.

#### 157. Synthesis of polyhydroxyketones.

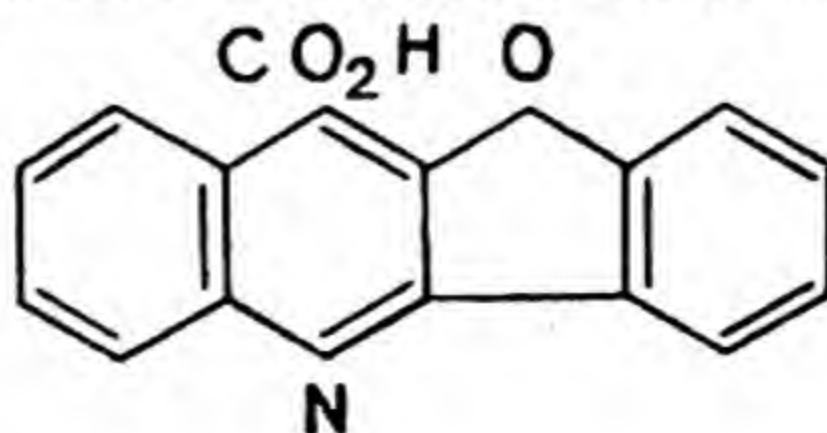
P. K. BOSE and SUNDAR RAM, Calcutta.

Iminochlorides, PhN : C(Cl)·R readily condense with polyhydroxyphenols in presence of HCl-ZnCl<sub>2</sub> to form products of the type R.C(:NPh)·R which are easily hydrolysed to the corresponding ketones. The yields are generally good and the method has been found useful for the synthesis of many naturally occurring ketones.

#### 158. Synthesis of atophan analogues.

P. K. BOSE and N. C. GUHA, Calcutta.

Coumaranone condenses with isatic acid in alkaline solution to form





which is structurally similar to atophan. This substance as also its derivatives are expected to possess valuable therapeutic properties.

159. Chloralides. Part II. The condensation of butyl chloral hydrate with  $\alpha$ -hydroxycarboxylic acids.

N. M. SHAH, Dharwar.

Recently Shah and Alimchandani (*J. Indian Chem. Soc.*, 1934, 11, 545) have studied the chloralides derived from the condensation of  $\alpha$ -hydroxy acids with chloral. But so far as the author is aware, no systematic work has been done with the butyl chloralides. The present investigation has been undertaken to study the butyl chloralides and their properties and compare them with those of simple chloralides.

Tartaric and citric acids have been condensed with butyl chloral hydrate in presence of conc.  $H_2SO_4$  and the condensation products have been studied. The work with other acids on the same lines is in progress.

160. The condensation of ethyl malonate with salicylaldehyde presence of organic bases.

P. N. KURIEN, K. C. PANDYA, and C. J. PETER, Agra.

Salicylaldehyde has been found (by P. N. K. and K. C. P.) to condense with malonic acid in presence of pyridine alone only when the base is present in traces. Knoevenagel (*Ber.*, 1898, 31, 2593; D.R.P., 97734) has condensed the aldehyde with ethyl malonate with a trace of piperidine.

The same condensation also occurs when traces of other bases are used: viz. pyridine, quinoline, isoquinoline, lutidine, naphthoquinoline, quinaldine, cinchonidine, dimethylaniline, and diethylaniline. Conditions of maximum yields (58%) are determined, the product being always ethyl coumarin-carboxylate.

161. Action of acetic anhydride on 2-acetyl-resorcin. A new method for the preparation of  $\gamma$ -resorcylic acid.

D. B. LIMAYE and G. R. KELKAR, Poona.

2-Acetyl-resorcin, m.p.  $157^\circ$  (Limaye and Gangal, *Ind. Sci. Congress*, 1934; Chemistry Section) by the action of acetic anhydride alone is converted into its diacetate, b.p.  $175^\circ-180^\circ/10$  mm.

In the presence of Na-acetate, however, 2-methyl-3-acetyl-5-hydroxy-chromone ( $C_{12}H_{10}O_4$ ), m.p.  $122^\circ$ , is formed together with its acetate ( $C_{14}H_{12}O_5$ ), m.p.  $109^\circ$ , and a substance melting above  $200^\circ$  which is under investigation.

The constitution of the chromone, m.p.  $122^\circ$ , follows from the products of its easy hydrolysis with caustic alkali, viz. acetone, acetic acid, and  $\gamma$ -resorcylic acid.

This furnishes an excellent preparative method for  $\gamma$ -resorcylic acid as judged from its purity and yield.

162. Synthesis of 3-(*o*-tolyl)-4'-methyl-7':8'-furo-coumarin and of 2-(*o*-toluoyl)-resorcin by the Nidhone process.

S. S. TALWALKAR, Poona.

(Communicated by D. B. Limaye.)

In continuation of Limaye's work on the Nidhone process (*Ber.*, 1932, 65, 375; 1934, 67, 12) the *o*-toluate of 4-methyl-umbelliferone (m.p.  $142^\circ$ ) obtained by the action of *o*-toluoyl chloride on 4-methyl-umbelliferone,



changes on treatment with aluminium chloride into 4-methyl-8-(*o*-toluoyl)-umbelliferone ( $C_{18}H_{14}O_4$ ), m.p.  $242^\circ$ , which on treatment with bromacetic ester gives the ethyl ester ( $C_{22}H_{20}O_6$ ), m.p.  $145^\circ$ , of the acid, 4-methyl-8-(*o*-toluoyl)-7-(carboxy-methoxy)-coumarin ( $C_{20}H_{16}O_6$ ), m.p.  $208^\circ$ ; which on treatment with acetic anhydride and sodium acetate gives 3-(*o*-toluoyl)-4-methyl-7':8'-furo-coumarin ( $C_{19}H_{14}O_3$ ), m.p.  $165^\circ$ .

The 4-methyl-8-(*o*-toluoyl)-umbelliferone when boiled with alkali yields 2-(*o*-toluoyl)-resorcin, m.p.  $119^\circ$ .

*o*-Toluic acid and resorcin give 4-(*o*-toluoyl) resorcin ( $C_{14}H_{12}O_3$ ), m.p.  $127^\circ$ , by Nencki's reaction.

### 163. Synthesis of 3-(*p*-toluoyl)-4'-methyl-7'-8'-furo-coumarin and of 2-(*p*-toluoyl)-resorcin by the Nidhone process.

G. S. SHENOLIKAR, Poona.

(Communicated by D. B. Limaye.)

In continuation of Limaye's work on the Nidhone process (*Ber.*, 1932, 65, 375; *Ber.*, 1934, 67, 12) *p*-toluoyl chloride is condensed with 4-methyl-umbelliferone to give a *p*-toluate of 4-methyl-umbelliferone,  $C_{18}H_{14}O_4$ , m.p.  $157^\circ$ , which on treatment with aluminium chloride yields a ketone, 4-methyl-8-(*p*-toluoyl)-umbelliferone,  $C_{18}H_{14}O_4$ , m.p.  $260^\circ$ . This ketone is condensed with bromacetic ester to form an ethyl ester,  $C_{22}H_{20}O_6$ , m.p.  $130^\circ$ , which on hydrolysis with alkali gives an acid, 4-methyl-8-(*p*-toluoyl)-7-(carboxymethoxy)-umbelliferone,  $C_{20}H_{16}O_6$ , m.p.  $188^\circ$ . The acid on treatment with fused sodium acetate and acetic anhydride yields 3-(*p*-toluoyl)-4'-methyl-7'-8'-furo-coumarin,  $C_{19}H_{14}O_3$ , m.p.  $175^\circ$ .

The 4-methyl-8-(*p*-toluoyl)-umbelliferone, m.p.  $260^\circ$ , when hydrolysed with alkali gives 2-(*p*-toluoyl)-resorcin,  $C_{14}H_{12}O_3$ , m.p.  $125^\circ$ , while the condensation of resorcin with *p*-toluic acid yields by Nencki's method, 4-(*p*-toluoyl)-resorcin,  $C_{14}H_{12}O_3$ , m.p.  $138^\circ$ .

### 164. A new method of the synthesis of phenanthrene and its derivatives.

N. N. CHATTERJEA, Calcutta.

A synthesis of hydroxyphenanthrene according to the following scheme is in progress.

When diphenic anhydride is reduced by means of sodium amalgam a lactide is formed, which when heated with potassium cyanide gives 2-cyanomethyl-2-carboxy-diphenyl. By the hydrolysis of this compound it is expected that the corresponding dicarboxylic acid will be obtained. The distillation of the lead salt of the dibasic acid or Dieckmann's reaction on the dibasic ester will give us the hydroxyphenanthrene.

The general importance of this new synthesis lies in the fact that the substituted phenanthrenes can be synthesised from corresponding substituted diphenic acids. It would be possible to synthesise phenanthrenes containing more than one hydroxyl group.

### 165. Synthesis of diphenyl derivatives. Part I.

N. N. CHATTERJEA, Calcutta.

A synthesis of unsymmetrical diphenyl derivatives having both the methyl and the hydroxyl groups attached to the nucleus is described. The process consists in decomposing the diazonium salts of benzene or toluene (*o*, *m*, *p*.) in presence of cresols (*o*, *m*, *p*). Symmetrical and unsymmetrical methyl derivatives of diphenyl ether are also produced as bye-products. The products may be isolated from the reaction mixture by distillation with superheated steam.



The general method employed in determining the constitution is to protect the hydroxyl group by methylation and then oxidising with permanganate the free methyl groups to the corresponding acids. By heating with soda-lime the acids lose carbon dioxide and the methoxy diphenyl derivatives, thus obtained, are easily identified as they are all known. The acetyl derivatives of these compounds have been prepared with acetic anhydride in presence of pyridine.

Investigations on the action of various reagents, e.g. oxalyl chloride, methylene chloride, ethylene bromide,  $\beta$ -ketonic esters, nitric acid on these new hydroxy-diphenyl derivatives are in progress.

166. Parachor and chemical constitution. Part II. The structure of the triphenylmethane dyes.

S. K. RAY, Calcutta.

Various formulæ have been proposed by different investigators as to the structure of the triphenylmethane dyes. That there is a fundamental difference in constitution between the colourless leuco bases and the deeply coloured dyes was recognised by many observers. The present work was undertaken to find out the constitution of the leuco bases as well as the coloured dyes. The surface tensions and densities of the leuco bases and the coloured salts of rosaniline, crystal violet and malachite green in various solvents have been determined and the parachor calculated. It was found that the colourless bases possess the benzenoid structure while the coloured salts are best represented by quinonoid configuration.

167. A synthesis of 1 : 2-diketones. The condensation of hexachloroethane with phenols.

S. K. RAY, Calcutta.

A synthesis of 1 : 2 diketones has been effected by a somewhat modified method of Reimer-Tiemann's reaction. Substituted phenols were found to react with hexachloroethane in presence of alkali yielding the corresponding diketones.

168. The condensation of chloral with thiourea and semicarbazide.

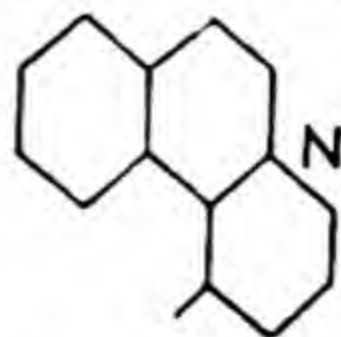
B. K. BANERJEE, Rajshahi.

The action of chloral hydrate upon urea and phenyl urea is known. Attempts have been made to condense chloral hydrate with thiourea-semicarbazide, etc. and monochloral-thiourea (m.p. 135-36°) and monochloral-semicarbazide (m.p. 212°) have been obtained.

169. Studies in isoquinoline series.

RANAJIT GHOSH, Calcutta.

Certain alkaloids, such as, emetine, cephaeline, etc. contain the



skeleton. Some interesting compounds containing this skeleton have been synthesised. Methyl-glutarolactonic acid chloride is condensed

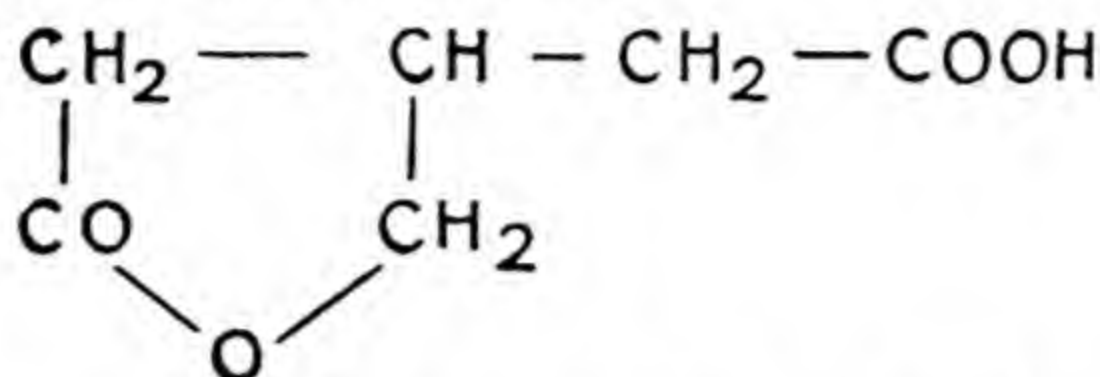


with  $\beta$ -phenyl ethylamine whereby the  $\beta$ -phenyl ethylamide derivative of the acid is obtained. The amide on treatment with phosphoryl chloride gives rise to an isoquinoline derivative. The isoquinoline base on reduction with zinc and acetic acid forms a piperidone which is now being subjected to electrolytic reduction for the synthesis of the above skeleton.

### 170. On the syntheses of certain $\gamma$ -lactonic acids.

RANAJIT GHOSH, Calcutta.

$\gamma$ -Lactonic acid of the constitution,



has been synthesised by treatment of one mol. of ethoxy acetaldehyde (obtained by the modified oxidation of ethylene-glycol monoethyl ether with sodium dichromate and sulphuric acid) with 2 mols. of malonic ester in presence of piperidine, followed by hydrolysis, decarboxylation and deethylation of the resulting compound (ethoxy-ethylidene-dimalonic ester). The reactive hydrogen atoms of ethoxyethylidene dimalonic ester may be replaced by alkyl groups by treatment with sodium ethoxide and corresponding alkyl halides, and the derivatives thus obtained on hydrolysis, decarboxylation and deethylation would give rise to a series of  $\gamma$ -lactonic acids. Hence this method may be considered as a general method of synthesis of lactonic acid of the above constitution. Some of these interesting derivatives have already been isolated by the author.

### 171. Action of amines on quinolinic acid. Part II.

A. K. DAS and INDUBHUSAN SARKER, Gauhaty.

It is an extension of the work on the action of aniline on quinolinic acid. In this paper the action of benzylamine, toluidines, and aminophenols has been studied under different experimental conditions. Generally, in all these cases, at first at ordinary temperature an additive compound with one molecule of the amine is formed and then with changed condition (e.g. by heating alone or with condensing agents) it loses molecules of water forming compounds corresponding to anilides and anils.

### 172. Studies in xanthone group.

A. C. SIRCAR and S. C. DUTT, Calcutta.

Preparation and properties of a good number of azo compounds from diazotised 3-amino-xanthone, and azo-methins obtained by condensing various aromatic aldehydes with 3-amino-xanthone are described. Finally, two new derivatives of xanthone, namely 3-iodo-xanthone and 2-nitro-7-iodo-xanthone have been prepared from the corresponding amino compounds *via*-diazo reaction.

### 173. A bitter principle from *Andrographis paniculata*.

S. S. GUHA SIRCAR and ABDUL MOKTADAR, Dacca.

The crystalline bitter principle from the leaves of *andrographis paniculata* (Kalmegh),  $\text{C}_{20}\text{H}_{28}\text{O}_5$  (approx.), has been obtained in a pure



form, m.p.  $220^{\circ}$ . It is an unsaturated hydroxy-lactone containing a methylene-dioxy-group, and is presumably related to a sesquiterpene. Its addition products with  $H_2$ ,  $HCl$ ,  $HBr$ ,  $ICl$ ,  $Br_2$ , and its reactions with  $POCl_3$ , phenylcarbimide and various oxidising agents and also with zinc dust and soda-lime have been carefully studied. Two hydroxy acids corresponding to the lactone, and their barium salts have been obtained in crystalline condition.

174. Chemical examination of *Tylophora asthmatica*.

N. N. GHOSH, I. B. BOSE, and SUDHAMOY GHOSH,  
Calcutta.

The drug is met with almost throughout India. The roots are reputed to act both as an emetic and as a cathartic. It is described as one of the best substitutes for ipecacuanha. Besides the presence of small amounts of oily matter, waxes, resins, tannins, potassium nitrate, etc., it was found to contain alkaloids. The amount of the total alkaloid obtained by assay was found to be about 0.44 per cent.

The total alkaloids isolated on a semi-large scale were found to consist of two alkaloids, both with feeble basic properties. Both were easily soluble in chloroform, but one was only sparingly soluble in absolute alcohol. The latter has been crystallised in irregular laminæ with a pale yellow color, m.p.  $265^{\circ}$ . This alkaloid has been termed *tylphorine*. The base has been analysed and several of the salts, such as hydrochloride, hydrobromide, hydriodide, sulphate, nitrate, etc., prepared in a crystalline state and their properties studied. The pharmacological action is under investigation. The second alkaloid, isolated from the mother liquors of the first, could not be obtained crystalline. It was a yellow, amorphous powder, m.p.  $130^{\circ}$  and was a very feeble base.

175. Molecular size of cellulose.

J. K. CHOWDHURY, Dacca.

The molecular weight of cellulose from different sources has been determined in very dilute solution by Staudinger method. The mol. wt. of cotton, jute, and bamboo celluloses in cuprammonium sols. are thus found to be about 1,44,000, 76,000, and 26,000 respectively. The number of anhydroglucose units in each molecule being 878, 516, and 189 respectively. In viscose, the numbers are 894, 468, and 158 respectively indicating slight disintegration. In acetylcellulose, the numbers are 138 units in the case of cotton and 86 in the case of jute cellulose, indicating considerable disintegration during acetylation. The number of glucose units in natural cotton must be higher than that obtained from cuprammonium solutions and must exceed 1000.

The molecular size of the above celluloses in viscose solution has also been determined with the help of Gibbs formula from changes of surface tension with time. The molecular area by cotton cellulose is found to be 571 sq. Å, that of jute cellulose 263 sq. Å, and that of bamboo cellulose 130 sq. Å.

176. Suitability of Indian bauxite for the manufacture of alumina by Bayer's process.

G. K. OAGLE and M. S. PATEL, Bombay.

Continuing previous work most of the samples of bauxite from important Indian bauxite deposits have been subjected to Bayer's process, and the yield of alumina has been determined. Best yields have been obtained from samples of bauxite from Kolhapur State and from the recently discovered bauxite deposit by one of the authors on the Tungar Plateau near Bombay in the Thana District.



Titanium oxide and iron oxide contents of the bauxite which have been found more suitable for the extraction of alumina by Bayer's process are such that it may be possible to utilise the 'red mud' obtained after alkali digestion for the recovery of titanium salts.

Experimental data has been worked out to determine approximately the cost of production of alumina on a commercial scale.

Experiments on the recovery of titanium oxide from the 'Red mud' are in progress.

### 177. Study of the changes in cashewnut shell oil on heating.

N. M. PATEL and M. S. PATEL, Bombay.

Cashewnut shell oil has been extracted by solvent process from raw cashewnut shells after the removal of the kernel from the nut. The solvent used was a fraction from ordinary motor petrol distilling below  $80^{\circ}$ . It has been found that by heating the oil in the atmosphere of nitrogen up to  $125^{\circ}$ , the saponification value, acid value and specific gravity decreases and iodine value increases with time and temperature. After heating the oil for  $1\frac{1}{2}$  hours at  $150^{\circ}$  in the atmosphere of nitrogen no further change takes place in the saponification value, acid value and specific gravity of the oil.

The raw extracted oil causes bestirs on human skin. The heated oil ceases to have this property. The raw oil dries more rapidly than the oil heated at higher temperature. Further work is in progress.

### 178. Preparation of banana or plantain flour.

M. S. PATEL, Bombay.

Drying of ripe plantains and preparation of flour from unripe plantains is being carried out as a cottage industry in the Thana and North Kanara Districts of the Bombay Presidency. Drying operations at these places are carried out by means of solar heat. The products are, therefore, not quite dry and are liable to be unhygienic as the time of exposure is about a week or more. The moisture content of the dried product reduces the keeping quality of the product considerably. Besides the product is neither crisp nor friable. The preparation of unripe plantains is also carried out under similar conditions. But as unripe banana does not contain high percentage of sugars, they dry fairly well. Fairly large amount of banana or plantain flour packed in sealed tins is being imported into this country and used as a medicinal diet. Improved and more hygienic processes for drying plantains into flakes and powder has been developed. Experiments to work out a data for designing a pilot plant are in progress.

### 179. Extraction of nicotine from tobacco.

M. S. PATEL, Bombay.

Black Leaf 40, a proprietary product containing nicotine sulphate as the principal ingredient, has been found by Bombay Department of Agriculture to be most effective for the control of aphids. It has also been found that nicotine in other forms also kills aphids. Black Leaf 40 is an American product and it is not available in India when required. Attempts are, therefore, being made to develop a process suitable for Indian conditions for the extraction of commercial nicotine from locally grown tobaccos. Various methods for the estimation of nicotine have been studied. Nicotine content of different varieties of tobacco grown, and commercial methods of nicotine extraction are being studied.



## 180. Drying of mango pulp.

M. S. PATEL, Bombay.

Continuing the previous work experiments have been carried out to work out the engineering data for the design of a pilot plant for the manufacture of mango pulp flakes or powder. The keeping quality of the mango flakes is studied. Samples prepared in the mango season of 1933 have not undergone deterioration. Further work is in progress.

## 181. Error in the estimation of morphine in opium by the process of British Pharmacopœia, 1932.

J. N. RAKSHIT, Gazipur.

Estimation of morphine in opium by former British Pharmacopœia process has been criticised by the author in *Analyst*, 1919, 337; 1921, 482; 1931, 711. Latest British Pharmacopœia of 1932 has introduced some alterations over the previous methods. Attempts have now been made in the present investigation to ascertain how figures obtained by the present method represent actual morphine content on opium.

## 182. Determination of reducing sugars by titration of acidic potassium chromate, potassium dichromate and alkaline potassium ferricyanide solution.

S. C. SEN and M. N. PHUKON.

A rapid method is described for the determination of reducing sugars by the direct titration with acidic: (1) potassium chromate solution, (2) potassium dichromate solution without using any indicator, and (3) alkaline potassium ferricyanide solution using methylene blue as an internal indicator.

The end point is observed in (1) and (2) by the sudden change of orange red colour of acidic  $K_2CrO_4$  and  $K_2Cr_2O_7$  solution to the green due to the liberation of simple Cr ion from the complex anions  $CrO_4^{--}$  and  $Cr_2O_7^{--}$ .

The end point in (3) is observed by the sharp change of the colour of the indicator methylene blue from deep blue to the colour of the original solution.

These methods give successful results both with grape sugar and laevulose. Attempts have been made to determine glucose in the original cane juice and agreeable comparative results have been attained with the usual Fehling's solution.

## 183. Influence of different reducing agents on one bath chrome liquor as regards (a) basicity, and (b) the quality of leather produced.

B. M. DAS, B. B. DHAVALÉ, and B. N. PAL, Calcutta.

With a view to find out how the basicity of one bath chrome liquor is affected by different organic and inorganic reducing agents used in converting bichromate acidified with sulphuric acid into basic chromic salt nine different chrome liquors were prepared by nine different reducing agents but keeping the amounts of bichromate and sulphuric acid the same in all of them. It was found that the basicities differed widely with different reducing agents.

Practical tanning tests were made with the nine different liquors and the characteristics of the final leather studied. It was found that the reducing agents materially affected the properties of the leather.



### 184. The estimation of small quantities of bromine by a new colorimetric method.

A. C. BOSE and K. N. BAGCHI, Patna.

A perusal of the literature does not show any work done on colorimetric estimation of bromine. The difficulty lies in the fact that bromine escapes from the standard solution and renders the matching useless. This has been overcome by using an aqueous solution of methyl orange as a stable substitute for bromine solution.

The method described in this paper consists in oxidizing a soluble bromide in acid solution with  $\frac{N}{50}$   $\text{KMnO}_4$  and dissolving out the liberated bromine with carbon tetrachloride and then matching it in a colorimeter against the standard methyl orange solution. The methyl orange solution is standardised by matching it against bromine from  $\text{KBr}$  solution of known concentration. The colorimetric reading (the standard being set at 20 mm.) thus obtained has been termed in this paper as *Colorimeter Factor* which will be the basis of all calculation for estimation of bromine in an unknown solution.

Calculation of result.—The colorimeter reading of the unknown solution with reference to the standard methyl orange set at 20 mm., is taken as the numerator and the colorimeter factor nearest to the observed reading (given in detail in the tables appended to the paper) and corresponding to the same strength of methyl orange is taken as the denominator. This is multiplied by the concentration of bromine in the known  $\text{KBr}$  solution (originally used for standardising the methyl orange solution) corresponding to the same colorimeter factor. Hence, the percentage of bromine in the unknown solution

$$= \frac{\text{Reading of the unknown}}{\text{Colorimeter Factor}} \times \text{Concentration of Br. (\%) in the bromide solution corresponding to the colorimeter factor.}$$

In all colorimetric estimations with a colorimeter of Duboscq type the standard is generally set at 20 mm. and is always taken as the numerator while the observed reading of the unknown as the denominator but in this method the usual arrangement has been reversed the explanation of which and also the deduction of the formula given above, have been described in the paper.

Apart from its intrinsic worth for estimation of small quantities of bromine colorimetrically, the importance of this method lies in the fact that an entirely different substance like methyl orange which has nothing in common with the substance to be estimated, can be utilised as a standard for colorimetric comparison and the usual method of calculation can be completely modified according to changed conditions. This method is, therefore, likely to throw more light in colorimetric field where the worker is often handicapped for want of a suitable standard.

### 185. Study of the exchange absorption in soil by velocity reaction.

S. C. SEN, Mushari.

The energy absorption of cations by the colloidal complex varies considerably. The absorption of the principal ions  $\text{Ca}^{++}$ ,  $\text{Na}^+$ , by artificially prepared soils containing  $\text{H} \cdot \text{Ca} \cdots$  and  $\text{Na}^+$  as the exchangeable cations has been studied.

The process of replacement of an absorbed ion by another in sol. is expressed by the monomolecular velocity reaction.

$$K = \frac{2.303}{t_y - t_x} \log \frac{(c)_\alpha - (c)_x}{(C)_\alpha - (c)_y}.$$



where  $(c)_x$ ,  $(c)_y$ , and  $(c)_z$  are respectively the content of the replaceable ion per gram absorbed in the system after the interval of  $x$ ,  $y$ , and  $z$  length of time. The duration of the complete reaction is short.

Both  $\text{Na}^+$  and  $\text{Ca}^{++}$  soils prepared from the artificial hydrogen soil and then replacement of  $\text{Ca}^{++}$  by  $\text{Na}^+$  and  $\text{Na}^+$  by  $\text{Ca}^{++}$  have been verified by the above reaction. The order of absorption from the velocity constant is in the order of  $\text{Ca}^{++} > \text{Na}^+$ .

The exchangeable capacities of other artificial soils are in progress.

186. On the variation of the oxidisability and acid values of Indian butter fat and their bearing on rancidity.

B. M. GUPTA and S. C. ROY, Lucknow.

Attempts have been made to find out the variation in the oxidisability and acid values of butter fat prepared under different conditions and the factors which influence these values. Efforts have also been made to find out to what extent these values can indicate the degree of rancidity.

187. On the relationship between the saponification value and the proportion of insoluble fatty acids of butter fat.

B. M. GUPTA and J. M. DHAR, Lucknow.

The ordinary tests for the determination of purity of butter fat usually depend on an estimation of the soluble and insoluble parts of volatile fatty acids. It appears that an examination of the insoluble acids can be utilised as an additional test for purity. It has been found that there is a relationship between the saponification value and the percentage of the fatty acids giving insoluble salts, and that for a definite value of the former there is a maximum value of the latter for all specimens of pure butter fat.

188. On the analytical constants of oils derived from certain varieties of mustard seeds grown in the United Provinces.

B. M. GUPTA and M. G. CHAKRAVERTY, Lucknow.

Although the investigations of Prain, Kinzel, Duthie, and Fuller have thrown a considerable amount of light on the characteristics of the different varieties of mustard seeds which are cultivated in India, there are still serious ambiguities so far as the vernacular names are concerned, and the 'Tori' of one district, may be the 'Lahi' of another, or the 'Sarson' of a third. Great difficulties are, therefore, experienced in collecting authenticated seeds. As mustard oil is an important article of food, a careful examination of the analytical constants of the oil derived from each variety separately is of great importance.

In the present investigation authenticated seeds of *Brassica campestris* Linn., *Brassica rugosa* Prain, *Brassica napus* Linn., and *Brassica Juncea* were obtained from the Divisional Superintendents of Agriculture and the specimens of oils derived were examined in accordance with the standard methods. Further examination will be made as soon as genuine seeds of other varieties can be procured.

189. Constitution of iodic acid and its salts. Part III.

M. R. NAYAR and L. N. SRIVASTAVA, Lucknow.

In the two previous papers (*Proc. Ind. Sc. Congress*, 1933, p. 199; *ibid.*, 1934) it has been shown from a number of considerations and experiments on freezing point, conductivity and Raman effect that iodic acid



in concentrated solutions is polymerized while in dilute solutions it has the simple formula of the monobasic acid  $\text{HIO}_3$  and iodates are derivatives of this last acid.

A further confirmation of the change in constitution of the acid with dilution is obtained from measurements of viscosity of iodic acid solutions from concentrations ranging from  $5N$  down to  $N/100$ . The graph obtained by plotting the logarithm of the molecular viscosity against the logarithm of concentration is nearly a straight line which changes its direction at about  $1 N$ .

190. Utilization of waste vegetation. Part I. Gasification of prickly pear (*Opuntia Dillinii*).

B. S. SRIKANTAN and S. RENGACHARI, Madras.

The sun-dried plant containing 16% of moisture and having a calorific value of 497 B.T.U. has been gasified by the Mond process to yield gases of high calorific value, ranging from 150 B.T.U. per cu. ft. to 425 B.T.U. per cu. ft. depending on the ratio of steam to air and the space velocity. About 60% of the nitrogen content in the plant is obtained as ammonium sulphate. The ash of the plant yields 25% of alkali chiefly  $\text{K}_2\text{CO}_3$  which is to be considered an important source.

191. A note on an examination of a mineral water in the Tinnevely District.

K. VENKATAKRISHNAYYA and S. RANGACHARI, Madras.

The geological characteristics of the locality is described. The spring water contains plenty of pure hydrogen sulphide and colloidal sulphur. The results of an examination for the mineral contents of the water are given.

192. Thermionic emission and catalytic activity. Part III. A mechanism of the activation of gases at hot metallic surfaces.

B. S. SRIKANTAN, Madras.

In part I (*Ind. Jour. Phys.*, 1931, V, VII, 685) the author has shown that catalytic activity of metals depends on their capacity to emit electrons at the temperatures at which chemical reactions are catalysed. In part II (unpublished) it is noted that a thoria ceria surface having 1% of ceria shows maximum thermionic emission than other mixtures. Swan (*J. Chem. Soc.*, 1924, 125, 780) finds that catalytic activity of this mixture is also maximum at this particular concentration. In this paper the two sets of observations are correlated and a mechanism of activation of gases at metallic surfaces is given on the assumption that adsorbed gases are activated in collision with freely moving electrons in the metal and that the velocity constant at any temperature is proportional to the saturation current at that temperature. An expression is derived connecting the velocity constant and temperature

$$K = Y T^{3/2} e^{-(b/T+X)},$$

where  $K$ =velocity constant,  $T$ =temperature,  $Yb$  and  $X$  are constants.

This equation has been tested for the decomposition of ammonia on tungsten and of nitrous oxide on platinum. Under simplifying conditions this equation reduces to that of the well-known but empirical equation of Arrhenius.



193. Sweet water fish oil. Part II. Liver oil of *Dhai fish*.

D. N. MAJUMDAR, Calcutta.

The preliminary examination of the oil has been done and the work on the separation of the constituent of the fatty acids is in progress.

194. Some inorganic preparations of the indigenous medicine. Part II. *Banga Bhasma* (Calcined tin).

R. N. CHOPRA, SUDHAMOY GHOSH, and A. T. DUTT, Calcutta.

This substance is believed to be a general tonic and alterative. It is used in the Hindu Medicine in diabetes, spermatorrœa, gonorrhœa, anæmia, asthma, gastric ulcer and various skin diseases, the dose being 1 to 4 grains. The material usually obtained is a dully grey amorphous powder with a slightly saline and metallic taste. A complete qualitative and quantitative analysis showed the presence of about 83% of oxide of tin together with silica, iron, alumina, lime, magnesia, potash, soda, chlorides, moistures and traces of other constituents. The amount of mineral matter soluble in the concentration of hydrochloric acid occurring in gastric juice was also determined and the constituents estimated. Clinical trials with the drug were carried out.

195. Some inorganic preparations of the indigenous medicine. Part III. *Lauha Bhasma* (Calcined iron).

R. N. CHOPRA, SUDHAMOY GHOSH, and A. T. DUTTA, Calcutta.

This substance is used in the Hindu Medicine in all forms of anæmia, general debility, tuberculosis, skin diseases and gastric and doudenal ulcer, the dose being 2 to 10 grains. The material obtained was an amorphous powder with a chocolate colour. It was subjected to a complete qualitative and quantitative analysis and found to contain about 91% of oxide of iron together with silica, lime, magnesia, phosphate, chloride, sulphate, and traces of potash and soda. The amount of mineral matter soluble in the concentration of hydrochloric acid occurring in gastric juice was also determined and the constituents estimated. The results of some clinical trials with the drug and their relationship with the constituents found are discussed.

## 196. An improved method for measuring optical rotatory dispersion.

R. PADMANABHAN, Bangalore.

The usual photographic method does not give accurate results with substances of low rotation and fails entirely for substances of little or no rotatory dispersion. The method described consists in combining such a substance with another of appreciable rotation and high dispersive power, when it becomes possible to determine the R.D. of the combination by the usual method. The R.D. of the latter is separately determined and by difference the R.D. of the substance of low rotation or low dispersive power can be found out. The usefulness of this method in working with dilute solutions in the vicinity of an absorption band is indicated and its applicability for substances of low dispersive power such as sodium tartrate and nopinene is illustrated in the latter case with readings and photographs.



## 197. Analytical uses of potassium mercuric iodide.

K. RAY, H. N. DAS GUPTA, and M. N. GOSWAMI, Calcutta.

In alkaline solution (NaOH) it helps us to distinguish aldehydes from ketones. The former gives black metallic mercury whilst the ketones are unaffected. The earlier statement of Gros (*Pharm. Chim.*, 1922, 26, 5) who examined few ketones and found that they also reduce, has been found to be inaccurate. Monohydroxy aldehydes like salicylic aldehyde, vanilin do not react, perhaps due to mercuration. Methylation restores the action as veratric aldehyde easily reduces. Potassium mercuric iodide solution made alkaline with sodium carbonate has been used by the authors for the quantitative estimation of glucose. The method is very simple. To about 35 c.c. of the reagent 50 c.c. of 10%  $\text{Na}_2\text{CO}_3$  solution and then the sugar solution are added and the mixture boiled for 5 minutes when the corresponding amount of Hg is formed. The solution is cooled and neutralised with acetic acid and iodine solution added. The excess of iodine remaining is titrated.  $\cdot 0045$  G. of glucose = 1 c.c.  $\frac{N}{10}$  Iodine.

## 198. On the catalytic activation of diastase.

SOBHANLAL BANNERJEE and H. K. SEN.

Following a work on synthetic enzymes, specially the action of phenyl amino acetic acid on pyruvic acid to simulate the enzyme carboxylase (*Proc. Institution of Chemists, India*), it was considered necessary to investigate if the carboxylase itself is activated by the addition of phenyl amino acetic acid or similar substances. With phenyl amino acetic acid, the activation of the carboxylase reaction of yeast is definite and a further activation was attempted by the catalytic action of the ultraviolet light. The result was not only not activating, but positively destructive. This was only to be expected, as the diastatic ferment in malt was known to be rendered completely inactive by the action of the ultraviolet light (Pincussen, *Biochem. Z* 134, 459, 1923; 141, 366, 1924; 152, 406, 416, 1924). The significance of such a destructive property of the ultraviolet light in therapy is obvious, but the discovery of protective reagents would be no less important, as the latter would increase the flexibility of the employment of such light in the science of actinotherapy. Accordingly, four sets of experiments were performed with malt diastase: (i) without catalyst, (ii) with catalyst, (iii) with catalyst and ultraviolet light and finally (iv) with ultraviolet light but without catalyst.

As a result of numerous experiments, it appears that asparagine, phenyl amino acetic acid, gelatine, tyrosine, aminobenzoic acid, ammonium citrate, exert varying degrees of protective action on malt diastase. Thus, exposure of 5 minutes to ultraviolet light (3,000 C.P.) and 12" arc at a distance of 2 feet, was just sufficient to completely destroy the diastatic activity of a sample of malt. If gelatine were added during the reaction, and the reaction tube exposed to the action of ultraviolet light exactly similarly for 5 minutes only, the diastatic power though reduced, was still found to be 15.16, as against 23.5 without the light. When exposed for 45 minutes, the diastatic value fell to 9.6. On the other hand, for the same period of 5 minutes, ammonium citrate of identical concentration and conditions of exposure gave the diastatic value 11. This shows that the protective action of gelatine is more than that of ammonium citrate. If gelatine be taken as a standard for comparison, a system of expressing the protective co-efficient may be introduced. But it is quite possible that certain substances function both as protectors and accelerators. For example, phenyl amino acetic acid, tyrosine, aminobenzoic acid, ammonium citrate are both accelerators and protectors. Whilst from the chemical nature of the accelerators, a surmise may be made as to the probable nature of the diastatic fraction of malt, the protective action



probably depends upon the capacity to absorb partially or wholly the destructive wavelengths of the ultraviolet light. Expressed in a slightly different way, the light acts selectively on these protectors, leaving the diastatic enzyme wholly or partially active. This appears to be plausible when we consider that gelatine, ammonium citrate and in fact many albuminoid substances are affected by the ultraviolet light. Further investigations are in progress.

199. The neutral oil and the phenol ratio in the low-temperature carbonisation tar of Indian coals.

S. S. GHOSH, H. K. SEN, and PROBHA BANNERJEE.

The ratio of neutral oils to the phenols in coal-tar is important from the point of view of its use in internal combustion engines. Addition of heavy boiling neutral oils to petrol appreciably increases the efficiency of internal combustion engines by the higher ratio of compression that can be used. The practically complete elimination of phenols by a single fractionation without the use of alkalies to neutralise the latter, would constitute a great improvement both by reducing the cost of fuel as also by creating a definite market for the low-temperature tar. On distilling some of the second class coals from Indian collieries, the neutral oil and phenolic oil ratio was usually found to be between 2 and 31/2. Distilling the coals, however, with a mixture of sodium carbonate, sodium acetate and iron filings, this ratio becomes as high as 5 to 7, meaning thereby that the proportion of phenolic bodies is very considerably diminished, rendering the once distilled tar fit for being used directly in internal combustion engines. Engine trials with a 25% mixture of the distilled tar with petrol are in progress.

200. A semi-technical apparatus for the saccharification of saw dust by pressure percolation.

B. D. GUPTA and H. K. SEN.

The importance of pressure percolation in the saccharification of cellulosic materials has been brought into prominence by the work of Schooler who claims a 90% conversion of cellulose into sugar by such an operation. The need for the verification of this and similar other statements being felt on a semi-technical scale, an apparatus was designed which was simple in its construction, and obviated the use of a boiler or spiral heater by the use of a set of ring burner. The pressure of steam inside the percolator was maintained uniformly at 10 to 12 atmospheres, whilst a 0.123% solution of sugar was continually tapped by percolating with a 0.5% sulphuric acid solution.

201. Recovery of sulphuric acid by bauxite in the saccharification of wood.

S. S. GHOSH and H. K. SEN.

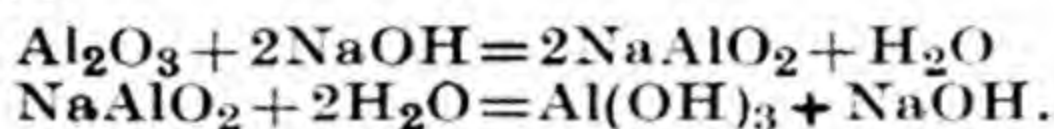
With 72% sulphuric acid, as is well-known, the saccharification of saw dust or indeed of any cellulosic material is complete, but the chief drawback of such a process for technically obtaining sugar solutions for fermenting into power spirit, lies in the removal and recovering of the very large quantity of sulphuric acid used in the process. The acid can be neutralised almost wholly by the addition of very finely powdered bauxite, supplemented by a small quantity of precipitated alumina, and the liquor concentrated under reduced pressure. When the concentration is such that the liquor shows signs of crystallisation, a quantity of alcohol is added to precipitate out all the aluminium sulphate retained in the sugar solution. After collecting the practically pure aluminium sulphate



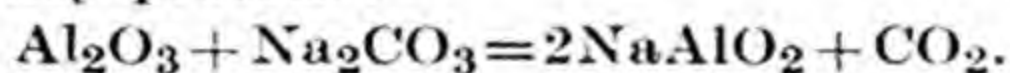
by suction or centrifuging and washing the precipitate with a little fresh alcohol, the combined filtrate is either used for the precipitation of aluminium sulphate in subsequent experiments, or is directly distilled to remove as much of the alcohol as possible. The residual liquor has now not infrequently a strength of 4 to 5% in its sugar content, which is then fermented by acclimatised yeast. The aluminium sulphate obtained in the process could be disposed of directly, or it could be roasted at about 850° C. when practically pure alumina remained behind, whilst the sulphur was quantitatively reproduced as sulphur trioxide, sulphur dioxide, and oxygen which could be used by converting the gas mixture into sulphuric acid by passing through a contact plant. The alumina obtained in the process could be utilised for the production of metallic aluminium, aluminous cement, or when a cyclic operation is intended, the same could be fused with sodium carbonate or sodium sulphate and carbon and re-obtained as precipitated alumina, to be used in the neutralisation of the sulphuric acid in preference to bauxite. In a cyclic operation, therefore, sodium carbonate would be a by-product, a feature of the process which deserves very serious consideration on account of the fact that there is no alkali industry in the country.

The following chemical reactions indicate the gist of the processes of recovery :—

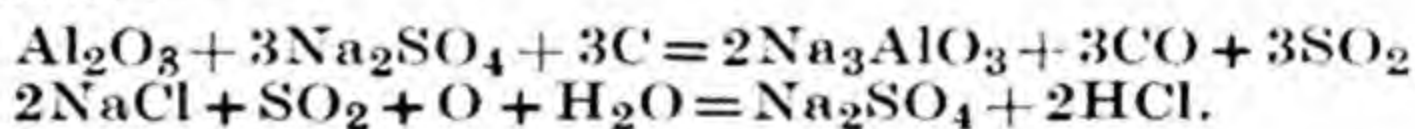
Bayer process :



Deville-Pechiney process :—



Peniakoff process :—



## 202. Studies in the lignocellulose group. Part VI.

BASUDEV BANNERJEE and H. K. SEN.

A significant fact has been observed in course of investigation in this line that chlorine peroxide solution does not remove all the lignin from saw dust, but about 6% of lignin still adheres to the cellulose isolated by the chlorine peroxide method. An oxymethyl determination of a specimen of cellulose so prepared, and that after removal of the cellulose by Willstätter process, showed definite presence of lignin, the percentage of  $\text{OCH}_3$  in the adhering lignin being about 8%. That this oxymethyl is not a characteristic of  $\beta$ -cellulose as maintained by Cross and Bevan (*Cellulose*, 1916, p. 93) is proved by the fact that all the cellulose isolated by the chlorine peroxide method does not go into solution on being treated with  $\text{HCl}$  (sp. gr. 1.2). There is reason to believe that a part of the methoxy in saw dust exists as methyl ester.

## 203. Synthesis of $\alpha$ -substituted cinchoninic acids through the Knoevenagel catalysts.

K. M. PANDALAI, Waltair.

The 3-substituted phenacylidiene oxindoles (I) obtained by the condensation of isatin and methyl ketones in presence of the Knoevenagel catalysts like diethylamine, piperidine, aniline and ammonia and subsequent dehydration in presence of dilute mineral acid cannot be converted into the 2-substituted cinchoninic acids (II) under the conditions of the Pfitzinger reaction (33%  $\text{KOH}$  and heat to 10 hours). This is evidently because these unsaturated oxindoles (I) have the *trans* configuration and are compounds formed without the hydrolytic opening of the oxindole



ring. These (I) could, however, be made to yield the  $\alpha$ -substituted cinchoninic acids (II) if geometrical inversion is effected of the *trans* isomer by the ultra-violet light method of Stoermer when the *cis* modification is formed and gives with dilute mineral acid the desired cinchophens (II). The Pfitzinger reaction, therefore, takes place presumably in three stages: (1) hydrolysis of isatin into *o*-amino benzoyl formic acid; (2) the reaction between the ketone carbonyl of the methyl ketone and the amino group of the *o*-amino benzoyl formic acid; and (3) elimination of a molecule of water from the carbonyl of the benzoyl formic acid and methyl in the methyl ketone effecting a ring closure giving the compounds of type (II). Thus it is evident that the 3-disubstituted oxindoles and the 3-substituted unsaturated oxindoles (I) are not intermediates in the Pfitzinger synthesis of substituted cinchoninic acids. The use of the Knoevenagel catalysts for condensation of isatin and methyl ketones and subsequent geometrical inversion of the *trans*-compound into the *cis*-compound followed by dehydration of the last with dilute mineral acid afford an excellent method for the synthesis of alkali sensitive quinoline derivatives from isatin avoiding strenuous alkali treatment.

#### 204. Adsorption and H-ion concentration. Part II.

N. A. YAJNIK, D. N. GOYLE, and J. R. JAIN, Lahore.

The adsorption of chrysoidine, acridine orange, water-blue and indigo-carmin from solutions of different pH by silica, alumina, and animal charcoal has been studied. It was found that the adsorption increases with the decrease of pH in the case of the acid dyes while reverse is the case with the basic dyes. On plotting the H-ion concentrations of the dye solution against adsorption a typical logarithmic curve is obtained in every case.

#### 205. Studies in sorption of gases by solids.

N. A. YAJNIK, D. N. GOYLE, and B. N. SIKKA, Lahore.

The sorption of hydrogen, oxygen, nitrogen, carbon dioxide and carbon monoxide by a number of metallic oxides, carbonates and sulphates and by some metallic nitrates, phosphates and sulphites has been studied. It was noticed that the solvent having a high sorptive power for one gas has generally a comparatively high sorptive power for the other gases as well and that on comparing the sorptive powers of the compounds of the elements belonging to the same group of the periodic classification it was noticed that the substances having lower molecular weights and lower molecular radii have higher sorptive powers.

#### 206. Use of brucine in volumetric analysis.

D. S. N. MURTY and T. R. SESHADRI, Waltair.

Brucine sulphate has been employed as internal indicator in estimations of (1) iron in its salts and ores and (2) organic matter in the soil when titrations with dichromate have to be carried out. The difficulties met with in the use of diphenylamine are avoided by this means and the end points determined more accurately.

#### 207. Relation between the sulphur content and the decomposition-points of Indian coals.

R. K. DUTTA ROY, Jamshedpur.

Very little efforts have so far been made to study the mechanism of caking process of Indian coals. Factors such as decomposition points, softening points, swelling curves, plasticity zone, etc. contribute a great



deal to a comprehensive understanding on the salient features of the formation of cokes. The decomposition point is just the critical limit when a coal in the destructive distillation just begins to give forth tar. The present study consists of a fairly elaborate investigation on the sulphur content and the decomposition point of Indian coals. The striking result is that there exists some definite relation between the percentage of sulphur and the decomposition point. Moreover, the sulphur content of coal is also a function of its geological age.

208. A relative study on the ultimate analysis of coal.

R. K. DUTTA ROY, Jamshedpur.

As it is evident, the ultimate analysis of coal plays an important rôle in the industrial valuation. It will considerably economise time and do away with the usual tedious laboratory methods if a workable and speedy relation be established with comparatively easier proximate analysis and the calorific value of coal. Efforts have already been made to establish such relation regarding the continental and American bituminous coal. The present study comprises a practicability of such possibilities regarding the Indian bituminous coal.

209. Formation and transformation of carbon ring compounds.  
Part III.

S. C. SENGUPTA, Calcutta.

The anhydride of *cyclohexane-1-carboxy-1-acetic acid* condensed with benzene in presence of aluminium chloride giving *cyclohexane-1-benzoyl-1-acetic acid* (m.p. 117-118°), this on reduction by the Clemmensen's method gave *cyclohexane-1-benzyl-1-acetic acid* (m.p. 93°). On cyclisation with 85% sulphuric acid this acid furnishes 1-keto-1:2:3:4-tetrahydronaphthalene-3:3-spirocyclohexane (b.p. 145°/3 mm.); this on again reduction by the Clemmensen's method gave 1:2:3:4-tetrahydronaphthalene-3:3-spirocyclohexane (b.p. 115-117°/3 mm.). This spiro hydrocarbon on selenium dehydrogenation at 300-350° gave phenanthrene and no methylphenanthrene or anthracene could be detected.

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ABSTRACTS OF PAPERS.

Section of Geology.

*President :—Dr. M. S. Krishnan, M.A., Ph.D.,  
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CALCUTTA.

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## Section of Geology.

### *Abstract.*

### GENERAL.

#### 1. Aerial reconnaissance.

P. EVANS, Digboi.

An illustrated lecture to be delivered by the author.

#### 2. Ancient gold mining and metallurgy in the Raichur district, Deccan.

CAPT. L. MUNN, Lingsugur.

An illustrated lecture describing the methods and processes used in the winning of gold in former times in parts of the Deccan.

#### 3. The evidence for a nappe in the Archæan (Sausar series) near Deolapar, Nagpur district.

W. D. WEST, Calcutta.

During the past 15 years Dr. L. L. Fermor and his party in the Central Provinces have mapped the Sausar series in great detail, subdividing it into a number of stages. This succession has been found to be constant over a fairly large area, and the determination of the geological structure from the distribution of these stages is therefore likely to be well founded. In this paper evidence is brought forward to show that around Deolapar, in the Ramtek tahsil of the Nagpur district, there occurs a sharp discordance in the succession, at which position one or more stages of the Sausar series are missing. The trace of the discordance is an irregular closed line, and it is clearly not a simple thrust. The details of the structure suggest that we have here a recumbent fold resting upon the surrounding rocks, from which it is separated by the discordance. Both the recumbent fold and the 'slide' upon which it rests have been further folded into a syncline.

Additional support for this view is provided by a study of the lithology. The Bichua stage, of which the recumbent fold is mainly composed, is rather different lithologically from the Bichua stage found in the adjacent rocks beyond the slide. The change of facies is too sudden to have been due to local variation in the sedimentation. But, taken in conjunction with the evidence for a slide, the difference is easily explained. It seems clear that the two sets of rocks (within and without the slide) were far separated at the time of their deposition, and have since been brought into juxtaposition with one another by horizontal movement along the slide.

#### 4. Palæoclimates in Northern India.

J. B. AUDEN, Calcutta.

Certain features relating to palæoclimates in Northern India are brought forward. These are:—



- (1) Arid or semi-arid conditions of climate probably attended the deposition of the following series :—  
     Peninsula ; Vindhyan and Panchet.  
     Salt Range ; Cambrian.  
     Himalaya ; Mandhali and Nagthat stages of Jaunsar series ; Upper stage of Tal series.
- (2) The existence of glacial beds or tillites in the Talchirs of the Peninsula, in the Tanakki boulder-bed of Hazara, and in the probably equivalent Blaini boulder-bed of the Simla-Mussoorie Hills.
- (3) The existence of wind-rounded sands in the Krol sandstone of the Simla Hills.
- (4) The existence of gypsum and anhydrite in the Krol limestone of the Simla-Mussoorie Hills.
- (5) The general absence of fossils from the pre-Tertiary rocks of the outer Himalaya ; their abundance in the rocks of the Tethys zone to the north.

The Himalaya may be divided into Peninsular Himalaya and Tethys Himalaya. Among the rocks present in the Peninsular Himalaya which bear direct relationship to those in Peninsular India may be cited the Gondwanas of the Eastern Himalaya in North Bengal and Assam, the Blaini boulder-bed of the Simla-Mussoorie Hills, the Gondwanas of Kashmir and the Tanakki boulder-bed of Hazara. Representatives of the Vindhyan may perhaps be found in the cystid-bearing limestones and associated phyllites and quartzites of the Chandragiri range in Nepal. The broad climatic changes, witnessed both in Peninsular India and in the Peninsular Himalaya, were :—arid conditions in the early Palæozoic ; glacial conditions in the late Palæozoic ; arid or continental conditions in the Mesozoic. The inversion temperatures of gypsum into anhydrite are discussed in relation to temperatures which may have prevailed during the deposition of the Krol limestone. Stringent conditions may have been partly responsible for the general absence of fossils from the rocks in the Peninsular Himalaya.

## 5. Caves in the Bhuban Hills, Cachar District, Assam.

P. EVANS and B. H. SINGH, Digboi.

The Bhuban Hills ( $24^{\circ} 40'$  :  $93^{\circ} 0'$ ) south-east of Silchar, provide good sections in the rocks of the Surma Series and have given their name to the Bhuban Stage of these beds. The hills attain a height of over 3,000 feet and the western face includes imposing cliffs of sandstones in the Upper Bhuban Sub-stage.

In a part of the hills where the arenaceous Upper Bhuban beds dip south-eastwards at low angles, there are two long narrow caves. A complete exploration of the caves has not been made, owing to difficulties of progress in their more remote parts. The paper gives a plan, sections, and photographs of the caves made during a survey of the accessible parts in December, 1933.

The caves occur in sandstone beds containing very little calcareous material and are strikingly unlike the caves found in limestone country. The total length of the two caves is over 1,600 feet ; they lie on approximately the same line and trend in a direction S.  $15^{\circ}$  E. The hills strike in a direction almost due south, appreciably different from the trend of the caves. Although the caves contain recent human remains, they are not artificial, and appear to be due to the enlargement of joints in the sandstone.



## STRATIGRAPHY AND PALÆONTOLOGY.

## 6. Recent Work on the Saline Series of North-Western India.

E. R. GEE, P. EVANS, and M. A. MAJEED, Digboi.

The age of the Saline series has long been the subject of controversy and recent fieldwork has led to definite evidence that the salt marl and associated beds are of Tertiary and not of Cambrian or Pre-Cambrian age. The paper describes the nature of the evidence obtained during the re-survey of the Salt Range, and discusses the micro-petrological evidence bearing on the age of the series.

## 7. Geology of the country in the vicinity of Bagh.

M. P. BAJPAI, Benares.

W. T. Blandford, in his memoir on Western India, mentions that a peculiar triangular tract near Bagh is occupied by the Bijawar Series. This tract has been sub-divided into shales and slates, dolomitic limestones, carbonaceous shales, black marble, conglomerate and Deccan Trap, and has been mapped on a scale of 1" to 1 mile by the present author. The bedding planes in the area are extremely obscure and the rocks have been highly cleaved, folded, and faulted. The greenstones which occur associated with shales and slates and the dolomitic limestones have been studied chemically and petrographically. The correlation of these Narbada valley rocks with the Bijawar and Delhi series is also discussed.

## 8. Some Local phases of Regional Metamorphism of Dharwar in the eastern portion of the Raichur Doab.

S. K. MUKERJEE and C. MAHADEVAN, Lingsugur.

During the mapping of the eastern portion of the Raichur Doab (between Lat.  $15^{\circ} 55'$  and  $16^{\circ} 30'$ , Long.  $76^{\circ} 55'$  to  $77^{\circ} 35'$ ) a band of Dharwar schists, not hitherto reported, has been traced, extending right across the Doab in a N.N.W. direction from the Tungabhadra to the Krishna river.

In this band, besides the normal hornblende and chlorite schists, (1) fine-grained diabasic, (2) granulated medium to coarse-grained, and (3) fine-grained siliceous, types could be recognized.

Structural and field relationships suggest that this band of Dharwar rocks has been subjected to great regional metamorphism.

The paper sets forth the results of the study of this band.

## 9. On the age and correlation of the plant beds in the Trichinopoly District.

C. PRASANNAKUMAR, Bangalore.

The existence of plant beds below the marine cretaceous rocks of the Trichinopoly District has been known from a long time. A review of the literature connected with these rocks shows that there has been no unanimity or preciseness in the age assigned to these beds and these have been merely mentioned as part of the Upper Gondwanas. During the course of a few recent visits the different exposures of these plant beds have been examined in detail, and the present paper embodies the results of these observations. The evidence gathered both in the field and from the fossil plants goes to show that these are best regarded as not much older than Lower Cretaceous (Wealden).



## 10. Notes on the Geology of Lower Cuddapah—II.

C. PRASANNAKUMAR and M. R. SRINIVASA RAO,  
Bangalore.

In a previous communication to this section of the congress in 1934, the authors have given a general account of the occurrence and stratigraphical distribution of the igneous rocks associated with Lower Cuddapah sediments. The present paper embodies the results of an intensive petrographic study of a portion of these igneous rocks (those belonging to Papagni Series) and their associates. Several interesting metamorphic effects accompanying this igneous activity have been described in detail and an attempt has been made to fix the grade and facies of this metamorphism.

## 11. An acaulescent fossil palm from Chhindwara District, C.P.

K. P. RODE, Benares.

This peculiar corn-like fossil plant specimen was obtained by the author during May, 1934, from Umaria, about 10 miles east of Chhindwara in the Central Provinces. This new plant-bearing locality is only 10 miles west of Mohgaon Kalan from where the author made a large collection of Intertrappean Flora during the last four years. The specimen, which is the only one so far discovered in this area, was not found *in situ*, but from the nature of its matrix, it can safely be taken as belonging to one of the Intertrappean bands outcropping in this locality.

In its external form the specimen is hemispherical with a roughly plane base and is traversed by several longitudinal depressions on the upper surface where the somewhat badly preserved internal tissues have been exposed. The transverse section, however, clearly shows under the microscope the typical palm structure, thereby enabling easy correlation with the fossil composite genus *Palmoxylon* Schenk. A close study of the structure as well as the form points to its being a new species and this has been named *P. umariensis*, after the locality.

12. On a dicotyledonous leaf impression : *Phyllites mohgaonensis*, sp. nov., from the Deccan Intertrappean Beds of Chhindwara District, C.P.

K. P. RODE, Benares.

The Intertrappean beds of Mohgaon Kalan, District Chhindwara, C.P., have yielded several leaf impressions of angiosperms. The author has described one of the dicotyledonous species from this collection.

The impression consists mainly of the top portion of originally a fair-sized leaf, roughly ovate in form with entire or undulate margin and obtuse apex. The venation is of the pinnate, net-veined type, with a stout straight mid-rib, and numerous secondaries and tertiaries. It compares closely with *Diospyros* and *Ficus* but its affinities are uncertain due to incomplete preservation.

Age :—Upper Cretaceous Intertrappean.

13. On the occurrence of a new Loxodontine form of Elephant in the Indian Cainozoic : *Palæoloxodon priscus* var. *bosei*.

D. K. CHAKRAVARTI, Benares.

Prof. Bose of Jammu, in a notice of some mammalian remains from the Siwaliks of Jammu, gives the figure of a part of a molar (R.I. 806) which appears to the present author to bear a very strong resemblance to a molar (No. 39370, British Museum) of *Elephas* (*Loxodon*) *priscus*



represented in fig. 7 of Plate XIV of the *Fauna Antiqua Sivalensis*. This latter form, established by Goldfuss in 1821 on some scanty material from England, was recognized by Falconer for a long time as a distinct species closely allied to the living African Elephant, but was later regarded by him as a form of *E. antiquus*. After comparing the Jammu form with *E. priscus*, *Palæoloxodon antiquus*, *Archidiskodon planifrons*, *Loxodonta africana*, and *Stegodon bombifrons* (to which Bose has referred the molar in question), the present author finds reasons to regard it as a variety of *E. priscus* Goldfuss.

14. On the generic reference of a doubtful rhynchorostrine bunomastodontid from Chinji in the Salt Range.

D. K. CHAKRAVARTI, Benares.

A left mandibular ramus (Amer. Mus., No. 19415) collected by Barnum Brown from near Chinji has been referred by Osborn to the genus *Rhynchotherium* on the basis of its apparently downturned rostrum. In the preserved portion of the specimen there is no evidence of downturning of the symphysis. The rostrum appears to be downturned, but it is evidently in an imperfect condition of preservation. The warping of the alveolus of the tusk appears to the present author to be a case of distortion superinduced upon the specimen after its entombment. This is corroborated by the nature of  $M_2$ , the grinding surface of which lies at a much lower level than that of the adjoining tooth,  $M_3$ . Hence there is no ground for referring this specimen to *Rhynchotherium*, a form confined to the south-western part of N. America. The author suggests that it should be named *Trilophodon angustidens* (Cuvier) var. *chinjiensis* (a name proposed by Pilgrim in 1913 for a hypothetical form to be discovered in the Salt Range area).

15. A new intermediate stage in the evolution of Indian *Stegodon* species.

D. K. CHAKRAVARTI, Benares.

A new stage in the evolution of Indian *Stegodons* is represented by a third lower molar (Plate XXXVII, fig. 2, *Trans. Geol. Soc.*, 2nd Ser., Vol. II) collected by Crawfurd from Burma and described by Clift under *Mastodon elephantoides*. This was later referred to *Stegodon insignis* by Falconer, who appears to have overlooked the differences between the characters of the specimen concerned and those of the type molar of *S. insignis*. The remaining part of the material under *M. elephantoides* was separated and assigned to *S. clifti*.

The present author proposes the name *Stegodon crawfurdi* for this form in honour of the pioneer explorer. The trivial name originally used by Clift cannot be used, because the type molar of *S. insignis* is more 'elephantoid' than the specimen under discussion, which represents a stage intermediate between *S. insignis* and *S. clifti*.

The author traces the affinity of this type from Burma with the type molars of *S. orientalis* Owen, *S. insignis birmanicus* Osborn, and a few others—all of which should be referred to the Burma form in consideration of its priority.

16. A note on the recent shore sands at Neendakara near Quilon.

K. Y. SRINIVASA IYENGAR, Bangalore.

The paper gives an account of the analysis of a sample of recent shore sands obtained at Neendakara near Quilon with special reference



to the mineral and faunal assemblage therein. The general composition of the sand is as follows :—

Quartz	..	..	61.6%
Calcareous matter	..	..	16.6%
Clayey matter	..	..	5.89%
Heavy residue	..	..	15.8%

Nearly 90% of the heavy residue is ilmenite, the rest being made up by zircon, monazite, and garnet.

Of the microzoa, the foraminifera are the most abundant—the most common forms being *Rotalia*, *Nonion*, *Triloculina*, *Spiroloculina*, *Elphidium*, etc.

### 17. Supplement to a Monograph of the Terebratulidæ of the British Chalk.

M. R. SAHNI, Calcutta.

The author has recently examined 335 Terebratulids collected zonally from the British Chalk, which collection was entrusted to him by the British Museum (Natural History) for investigation. With few exceptions, all the Terebratulids investigated fall under the subfamily *GRYPHINÆ* Sahni. For the reception of certain genera, with divided inner hinge-plates, like *Terebratula* Muller s. str., *Neoliothyris* Sahni, *Rectithyris* Sahni, a new subfamily of the Terebratulidæ is proposed to be established. The author claims that he has established a satisfactory basis of classification for the Upper Cretaceous Terebratulid species, and that the same classification can be extended to separate stocks of Jurassic and Tertiary age.

## MINERALOGY AND PETROLOGY.

### 18. A quartz-garnet intergrowth with the outer form of garnet.

A. K. ROY, Calcutta.

The specimen is a portion of a fairly big crystal of garnet and measured 4" × 4" × 3". It was obtained from a pegmatite dyke, north of Gujandi, Gaya District.

Although it exhibits the characteristic form of garnet, the interior has an excellent graphic intergrowth of garnet and quartz. The approximate ratio between garnet and quartz, as calculated from the specific gravities, is 73 : 27. The graphic intergrowth appears to be due to eutectic crystallization.

### 19. 'Blue Amphiboles' from Mysore.

P. R. JAGAPATHY NAIDU, Bangalore.

Frequent reference has been made in the Records of the Mysore Geological Department to the occurrence of 'Blue Amphiboles' in various kinds of rocks in Mysore. These blue amphiboles have now been studied by the author and it has been shown that they vary from actinolite through basaltic hornblende to glaucophane, with an appropriate mineral suite of metamorphic origin like garnet, deep brown biotite and epidote. The exact mode of origin of these blue amphiboles is also different in different places.



20. Petrological notes on some of the rock types of Kalmali, Kallur, Nilagal, and Ganekal hills, Raichur District.

L. S. KRISHNAMURTHY, Lingsugur.

In the Dharwar band described by Mukerjee and Mahadevan, some prominent hills occur near Kalmali (Lat.  $16^{\circ} 11' 52''$ , Long.  $77^{\circ} 12' 50''$ ), Kallur (Lat.  $16^{\circ} 8' 29''$ , Long.  $77^{\circ} 11' 49''$ ), Nilagal (Lat.  $16^{\circ} 11' 52''$ , Long.  $77^{\circ} 8' 0''$ ), and Ganekal (Lat.  $16^{\circ} 14' 0''$ , Long.  $77^{\circ} 7' 3''$ ).

These hills consist of rock types with granulitic structure, containing apatite, pyroxene, micas, and other ferromagnesium minerals and sometimes blue blebs of quartz. The paper describes the petrological characters of the representative types.

From magascopic and microscopic characters, the affinity of these to the so-called 'pseudo or quasi-Charnockites' described by the Mysore Geologists is discussed.

21. Porphyritic dykes in parts of Raichur and Manvi Taluqs.

C. MAHADEVAN, Lingsugur.

In the southern parts of Manvi and Raichur Taluqs, Raichur Doab, a large number of dykes have been traced with a N.W. to S.E. trend, most of them being very long. They occur near the junction between the Dharwar schists and the gneisses of the crystalline complex.

One of these dykes which is normally doleritic in character, shows porphyritic feldspars and quartz, for a distance of about 6 miles. To the south of this, another dyke which is also normally doleritic, becomes locally siliceous and for a distance of about 3 miles includes xenoliths of gneisses and vein quartz.

The paper discusses the field relationship, structural peculiarities, and microscopic characters of these two abnormal members of this group of dykes.

22. Dyke rocks of Gudwal Samasthan, Raichur District.

H. S. KRISHNAMURTHY and L. S. KRISHNAMURTHY,  
Lingsugur.

Numerous dykes, mostly of doleritic nature, are found traversing in a W.N.W.-E.S.E., and rarely also in a N.-S. direction. They are of post-gneissic age, but there is no stratigraphic evidence in this area to define their upper limit.

The paper discusses their mode of occurrence, age, and petrological characters.

23. A note on the Arakere granite (Mysore).

B. N. RAGHUNATHA RAO, Bangalore.

The paper deals with a detailed study of the small east-west granitic hills near Arakere, a small village in Mandya Taluk. This granite is distinctly intrusive into the gneisses, hornblende schists, and quartzites which form the country rock; and the intrusion appears to be of the laccolithic type. On a careful examination, three distinct facies of the granite have been distinguished: (1) the pale pink to grey coloured normal granite, (2) the graphic granite with a deep pink colour, and (3) the hornblendic grey diorite-like rock, the last one showing evidences of contamination. The relation of this granite to the felsite and porphyry dykes extensively found in this area has also been discussed.



24. Petrography of some gneisses and associated basic rocks of the Santal Parganas, Bihar.

S. K. RAY, Calcutta.

The paper contains a preliminary petrographical account of some rocks which occupy the country extending north and south between Deoghar and Jasidih in the Santal Parganas, Bihar.

The rocks fall into two broad groups, one acid and the other basic. The acid group includes foliated biotite-hornblende-gneisses and hornblende-pyroxene-bearing granulitic rocks, together with quartz-felspar rich types of aplitic, pegmatitic, and sub-pegmatitic nature. There are local augen and porphyritic felspar-bearing variants of the gneisses. The pegmatitic bodies cross all the above rocks (and some rocks of the basic group) in the form of dykes or less regular patches. The mutual relationship of the gneisses, the granulites, and the quartz-felspar-rich types is not clear; the pegmatitic bodies are occasionally seen to pass into them with imperceptible gradation.

The basic group comprises amphibolites and other melanocratic rocks which are composed of hornblende, monoclinic and rhombic pyroxene, biotite and plagioclase. They occur within the acid suite as clean-cut bands of variable shapes and dimensions, and as larger and more irregular dyke-bodies or domes. Isolated fragments of faulted basic bands and xenoliths of some basic rocks are also found, and morphological variations and peculiarities presented by the former form the most conspicuous feature of this interesting area.

25. Petrological classification of the Dome Gneiss of Kodarma.

S. K. ROY and N. C. NANDY, Dhanbad.

26. Geology and petrology of the Mica Peridotite of Kodarma.

S. K. ROY, N. C. NANDY, and N. PRASAD, Dhanbad.

27. The heavy minerals of the Erinpura Granites and Microgranites of Danta State, Gujarat.

N. L. SHARMA and S. PURKAYASTHA, Dhanbad.

28. The Raniganj anorthosite.

S. C. CHATTERJEE, Patna.

The Raniganj anorthosite covers an area of approximately 100 sq. miles and extends across the southern part of the Raniganj coal-field in the districts of Bankura and Manbhum. In the latter district it shows definite intrusive relation to the Archæan complex.

There are associated granite and norite dykes and contemporaneous veins, and all the three rocks anorthosite, norite, and granite—belong to the same Petrographical province.

The structural relations of the three chief rock types are discussed in relation to their bearing on the mode of origin of the anorthosite body. Results of chemical and microscopic studies are also indicated.

29. On the occurrence of an ultra-basic rock in the Raniganj coal-field.

N. N. CHATTERJEE, Calcutta.

In the paper the author has described one ultra-basic rock occurring in the Jamuria area of the Raniganj coal-field. The rock is found to be



intrusive into the Raniganj coal-measures. The coal lying in the adjoining locality has been appreciably damaged and converted to *jhama*. One of the interesting features of the rock is the presence of patches of felspar about an inch in length. The physical and chemical characters of the rock are discussed in the paper.

### 30. Petrology of the Igneous Rocks of the Bijawar Series.

M. P. BAJPAI, Benares.

Geological mapping of an area, about 16 miles long and 11 miles wide in the central portion of the type area, reveals that igneous rocks are of frequent occurrence in the series. Palda, Surajpura, Sarwa, and Rampura are some of the new localities of their occurrence. The rocks are medium-grained quartz-dolerites. Late crystallization of iron-ore is shown by the inclusion of felspar and pyroxene in magnetite. Four chemical analyses show that the rocks are richer than the Deccan Traps in soda. In these two respects the Bijawar dolerites closely resemble the Gwalior Traps previously studied by the author.

### 31. Field description of some of the occurrences of Igneous Rocks of Cutch.

M. P. BAJPAI, Benares.

A period of about 7 months was devoted to the study of the igneous rocks of the mainland of Cutch during the field-season, 1933-34. The paper describes some of their important occurrences and structural characteristics. Petrographic and chemical description of rocks, which have so far been studied, has also been included. The study shows that there had been two phases of igneous activity in Cutch, one basic and the other ultra-basic.

### 32. Preliminary study of some lava flows of the Rajmahal Hills.

N. P. KATAKI, Calcutta.

In the paper the author has described the petrographical features of the basalt flows occurring in the neighbourhood of Pratabpur (Lat.  $25^{\circ} 7' 43''$ ; Long.  $87^{\circ} 22' 21''$ ) and Goradi (Lat.  $25^{\circ} 6' 15''$ , Long.  $87^{\circ} 25'$ ). Field evidences have shown that there are seven distinct flows in the neighbourhood of Pratabpur and five in the Goradi region. The microscopic examination of the basalts shows that the primary constituents include plagioclase felspar, augite, magnetite, and glass. The secondary minerals consist of chlorophæite, chabazite, calcite, and palagonite. The rocks are porphyritic with the phenocrysts of felspars which show sometimes zonary banding. The flows differ from one another in the coarseness of the minerals and in the amount of glass. The nature of some of the intertrappean beds is also dealt with. The author has suggested some correlation of the lava flows of these two regions.

### 33. On the occurrence of scoriaceous lava in the neighbourhood of Simra in the Rajmahal Hills.

N. N. CHATTERJEE, Calcutta.

The author of this paper collected several specimens of highly porous and vesicular basalt lava from Simra (Lat.  $25^{\circ} 2'$ ; Long.  $87^{\circ} 21'$ ) and its neighbourhood in the Rajmahal Hills. The basalt layers are found to rest on the infra-trappean bed of white shale which has been sufficiently baked due to the contact effect. Several fragments of quartz and shale are found to have been entangled in the extrusive rock. The overlying



portions of this scoriaceous rock consist of coarsely granular and porphyritic basalt with augite and felspar as the chief constituents. The phenocrysts have lamellar twinning and zonary structure. The paper deals with the physical and chemical characters of this vesicular slaggy basalt in detail and with its field relationship. An attempt has been made in the paper to correlate these with the basalt flows of the adjoining localities.

### 34. Some observations on the diamond-bearing rocks of Banganapalli and Wajrakarur.

K. RAJAGOPALASWAMY, Madras.

All the diamond-bearing rocks of India belong to the Vindhyan System, the diamonds occurring mostly in two distinct conglomerate horizons, the upper one being productive in N. India and the lower one in S. India. The two most important diamond localities of South India are Banganapalli and Wajrakarur. At Banganapalli the diamonds occur *in situ* in the basal conglomeratic strata of the Kurnool Series. The productive layer, which is only a few inches thick, is a shaly or sandy conglomerate containing pebbles of quartzite, jasper, and shale, the heavy mineral suite revealing magnetite, ilmenite, rutile, zircon, and apatite. The diamonds seem to have been derived by weathering from certain trap-sills intrusive into the Vainpallis and the Cheyairs. An examination of these igneous rocks shows them to be composed essentially of augite and basic felspar. A quantitative mineralogical estimation of this rock has been made and its composition calculated therefrom.

At Wajrakarur the occurrence of diamonds is rather peculiar, there being no definite diamond-bearing bed as at Banganapalli. There is, however, a remarkable volcanic neck around which diamonds are picked up regularly. This neck has only a superficial resemblance to the Kimberlites of South Africa. No diamonds have ever been found in the tuff material itself so that it is difficult to regard this neck as the source of diamonds. M. Chaper has put forward the theory that the diamonds have been derived from the pegmatite veins that penetrate the country rock. Such an idea is untenable since there are scarcely any pegmatites in and around Wajrakarur. But there are isolated outcrops of decomposed basic igneous rocks which seem to be of the same age as the trap-sills of Banganapalli and are also similar to them in mineralogical composition.

That the diamonds should occur only in the Vindhyan all over India is more than a coincidence. They are always in close proximity to granitic, gneissic, and schistose area penetrated by basic dykes of Bijawar age (the equivalents of the South Indian Cheyairs). It is therefore suggested that the basic dykes of Bijawar age are the home of Indian diamonds.

## ECONOMIC GEOLOGY.

### 35. On the occurrence of Mica at Gurpa, Gaya.

M. P. BAJPAI, Benares.

Pegmatitic veins rich in mica occur in the neighbourhood of Gurpa, a railway station on the East Indian Railway, about 25 miles south-east of Gaya.

Three veins running parallel to one another were traced for a length of 9 miles. The paper contains a description of Mica, the country rocks and the accessory minerals, and discusses the possibility of developing this area. The discovery of mica at Gurpa extends the Bihar Mica Belt by about 14 miles westwards.



## 36. The use of nepheline syenite in the glass industry in India.

V. S. DUBEY and P. N. AGARWAL, Benares.

The two deposits of nepheline syenite in Northern India are found in the Girnar Hills of Kathiawar and in the Kishengarh State in Rajputana. Pegmatoid varieties are also associated with them. So far, these rocks have been used only as road metal. Their average composition is : silica 56 per cent., alumina 20, total iron 4, soda 9, potash 5, lime 2, magnesia 1, and other constituents 3 per cent. This investigation was taken up with a view to reducing the cost of glass manufacture by substituting nepheline syenite rock as the source of soda instead of imported soda-ash. The cost of the rock containing 14 per cent. of alkalis is about 8 annas per cwt., while that of soda-ash with 58 per cent. of the same is about Rs. 7 per cwt. Thus, for getting the same amount of alkalis out of the rock, the cost will be only about Rs. 2.

Glass of the following batch composition—sand 100 parts, rock 100 parts, lime 25 parts, and sodium carbonate 25 parts—has been found to be satisfactory and can be melted at 1,250°C. and easily blown. The iron-free pegmatite gives an almost white glass, while the ordinary rock gives a bottle-green glass because of its containing ferro-magnesian minerals. The removal of such minerals from similar rocks has been accomplished in Russia, and attempts are being made to evolve a process here. The success of such a process will make billions of tons of this rock available for glass manufacture in this country.

Alumina imparts several good properties to the glass, such as lustre, resistance to chemical action and mechanical shocks, reduction of the tendency to devitrification and better annealing properties. It has been found that the introduction of alkali through the nepheline syenite rock gives a glass which is less viscous than that got by using orthoclase felspar.

## 37. Occurrence of Bauxite in the Thana District, Bombay.

M. S. PATEL, Bombay.

Dr. Fox has stated in his monograph on bauxite that there is possibility of finding aluminous laterite beyond Bassein Creek, on Kamandurg hill and on the tableland of Tungar in the Thana District of the Bombay Presidency. The area has been investigated. High grade bauxite has been found on the Tungar hill. Bauxite occurs on the scarps of the Tungar plateau in the form of boulders about 10 to 15 feet from the top under an overburden of ferruginous laterite. The analysis of the samples is as under :—

		A	B	C	D	E
SiO <sub>2</sub>	.. ..	9.66	4.25	2.75	0.62	1.02
TiO <sub>2</sub>	.. ..	4.15	4.02	1.84	4.68	6.21
Al <sub>2</sub> O <sub>3</sub>	.. ..	47.95	54.42	52.99	57.08	55.14
Fe <sub>2</sub> O <sub>3</sub>	.. ..	3.95	7.87	13.49	5.00	5.11
MgO	.. ..	1.49	trace	trace	trace	trace
CaO	.. ..	trace	trace	trace	trace	trace
Loss on ignition	.. ..	32.78	29.35	29.88	32.2	32.63
TOTAL	.. ..	99.98	99.91	101.05	99.58	100.11
Sp. Gr.	.. ..	2.4	2.22	2.3	2.29	2.16



The investigation that has been done so far indicates that there is a possibility of finding an adequate deposit of bauxite for the manufacture of aluminium. A navigable creek is found about 3 miles from the deposits and so it will be possible to transport the mineral in barges to Bombay or Kalyan, a distance of about 60 miles. The cost of transport from the wharf on the creek to Bombay or Kalyan is likely to work out at Rs. 0.7 per ton. A firm in Bombay has applied for prospecting licence.

38. Occurrence of natural gas in Broach District, Bombay.

M. S. PATEL, Bombay.

From the casual geological observations made by the author in connection with his investigation work regarding the occurrence of natural gas at Gogha, Ahmedabad District, Bombay, he found that there was a possibility of the gas field extending on the other side of the Gulf of Cambay round about Broach. The area has been investigated and natural gas has been located in a *kund* at Hajad, a village in the Ankleshwar Taluka of the Broach District. The gas has been found to contain about 94% combustible gases calculated as methane. If found in adequate quantities the gas will be a very cheap source of power and heat to the adjoining industrial centres of Broach, Ankleshwar, and Surat. A firm in Bombay has been granted prospecting licence.

39. A note on the bore-hole logs in parts of Aurangabad and Parbhani Districts discussed in relation to the distribution of underground water in the Deccan Traps.

C. MAHADEVAN, Lingsugur.

The conclusions arrived at by Capt. Leonard Munn regarding the distribution of underground water in Deccan Traps (*Journal, Hyderabad Geological Survey*, Vol. II, pp. 89-102) were further verified from the examination of the bore-hole records maintained by the Agricultural Department of H.E.H. the Nizam's Government and by actually visiting the sites of the wells in Aurangabad and Parbhani Districts of the Hyderabad State. The paper describes the results of this study.

40. Action of certain solvents on some Indian vitrains.

N. N. CHATTERJEE, Calcutta.

The author has carried out in the laboratory some experiments on the action of pyridine and chloroform on some Indian vitrains. The specimens include (1) Vitrain from Korea State coal; (2) Vitrain from Kargali seam, Bokaro coal-field; (3) Vitrain from South Karanpura coal. The specimens are all of Barakar age. Several specimens of Tertiary vitrains obtained from Watching and Tipongpani coals, Upper Assam, and from Namma and Kalewa coals, Burma, were also subjected to the solvent action of pyridine and chloroform. The alpha, beta, and gamma compounds have been determined quantitatively in all these specimens and the relationship between these extracts and the caking and swelling properties has been discussed in the paper.

41. A short note on the sulphur compounds in some of the coal specimens from Upper Assam.

N. N. CHATTERJEE, Calcutta.

In a previous communication the author described the high grade Tertiary coals of Upper Assam and recorded the occurrences of different



sulphur forms in them. The present paper embodies the result of further study in that direction and includes Watching, Tipongpani, and Namdang coals which are all of Miocene age. The distribution of the sulphide and sulphate forms of sulphur in the specimens of coal before and after high temperature carbonization has been discussed in the paper.

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ABSTRACTS OF PAPERS.

· Section of Chemistry.

*President ;—Dr. P. C. Guha, D.Sc.*

CALCUTTA.

ASIATIC SOCIETY OF BENGAL, 1, PARK STREET.







## Section of Chemistry.

### *Abstracts.*

#### INORGANIC CHEMISTRY.

1. Resolution of co-ordinated inorganic compounds. Part III: Active cadmium propylenediamine salts.

PANCHANAN NEOGI *and* K. L. MONDAL, Calcutta.

The work commenced by Neogi and G. K. Mukherji had to be repeated owing to the lamented early death of Mr. Mukherji. Co-ordinated cadmium salts with both *d*- and *l*-trispropylenediamine have been isolated.

2. Salts of gallium : Part I.

PANCHANAN NEOGI *and* S. K. NANDI, Calcutta.

Several new salts of gallium have been prepared.

3. Complex compounds of biguanide with tervalent metals : chromium and cobalt.

P. R. RÂY *and* HARIBOLA SAHA, Calcutta.

Though the complex biguanide compounds of bivalent copper, nickel, and cobalt have been described long ago, the constitution of the complex metal-biguanide ion is still under dispute. In order to elucidate this unsettled problem the authors have prepared and studied the properties of biguanide complexes of tervalent chromium and cobalt. These compounds, which have not yet been described in the literature, form beautiful ruby-red crystals—the colour being more prominent in the case of chromium complex. They are strong bases. Three molecules of biguanide are co-ordinated with each metallic atom—the biguanide acting as a bidentate group. The co-ordination number of the metal atom in these complexes, as well as their physical and chemical properties, throw a flood of light on their constitution and those of biguanide complexes in general.

4. Complex metal-ammonium selenites and selenito-metal-ammines.

P. R. RÂY *and* A. B. GHOSH, Calcutta.

A number of complex metal-ammonium selenites and selenito-metalammines have been prepared. All the latter contain cobalt as the central atom, and the selenito group occupies in them only one co-ordination position like the corresponding sulphito group. Unlike the sulphito complexes, however, these are readily hydrolyzed giving rise to aquo-compounds. Co-ordinating capacity of the selenito group is, therefore, very weak, possibly due to its larger volume.

Among the metal-ammonium selenites, compounds with cobalt, nickel, and copper as the central atoms have been prepared.



## 5. Analysis of ilmenite.

K. R. KRISHNASWAMI, Bangalore.

The volumetric determination of iron in ilmenite by reduction with hydrogen sulphide does not give reliable results unless the concentration of sulphuric acid during reduction is kept within narrow limits.

The following method has been found to give satisfactory results and is also rapid in execution. One part of the ilmenite solution is reduced and titrated with standard ferric sulphate solution in the usual manner (thiocyanate indicator), and another part of the solution is similarly reduced and titrated with the usual precautions with standard permanganate. The two titrations furnish the data required for the calculation of the iron and titanium contents of the sample.

## 6. Helium content of some Indian rocks and minerals.

M. R. A. N. RAO and K. R. KRISHNASWAMI, Bangalore.

The measurement of the helium liberated from some Indian minerals on heating has been carried out with the help of the apparatus described previously. (The gas from Indian Oil wells, *J. Ind. Inst. Sc.*, 1934, III).

The specimens were heated to a temperature of 1100–1150°C. in a furnace operated with 'Silit' rods.

Ten determinations with three different samples of monazite from Travancore gave the average value 0.931 c.c. helium per gram of mineral.

## 7. The action of hydrogen sulphide on barium and mercurous chromates.

M. A. HAMID, V. S. BHATIA, and H. B. DUNNICLIFF, Lahore.

Purified hydrogen sulphide was bubbled through suspensions of the chromates in water. Barium chromate gives a precipitate containing the hydroxide, thiosulphate (co-ordinated), sulphate (co-ordinated), barium sulphate (traces), and sulphur. The filtrate contains barium thiosulphate and polysulphide. Tetrathionate was not detected as an intermediate or bye product. At 80–85° the sulphate increases and thiosulphate decreases.

At low temperatures, sulphite is detected among the products of reduction of mercurous chromate, but none is found when the gas is passed at 80–85°C.

## 8. The slow oxidation of hydrogen sulphide in aqueous solution.

H. B. DUNNICLIFF, Lahore.

Hydrogen sulphide is decomposed freely, giving water and sulphur. Sulphur reacts with water forming sulphylic acid ( $\text{H}_2\text{SO}_2$ ) and hydrogen sulphide. The sulphylic acid is oxidized to sulphurous acid which may combine with either oxygen or sulphur giving sulphate or thiosulphate. In some cases, both of these reactions proceed simultaneously but the fate of the sulphurous acid depends upon the nature of the bases present, sulphide being completely suppressed in alkaline media, giving thiosulphate, and in feebly or strongly acid media containing a moderate concentration of oxidizing agents, giving sulphate.

Side reactions show that, in certain circumstances, dithionate can be formed from sulphite and tetrathionate by the mild oxidation of thiosulphate.

It is most improbable that thiosulphate is formed by the condensation (with loss of one molecule of water) of two molecules of sulphylic acid



or that sulphate is the result of the hydrolysis of the thiosulphates of weak bases.

9. Electro-deposition of chromium from potassium dichromate baths. Part I: In presence of sulphate.

S. R. PATHAK and S. HUSAIN, Hyderabad (Deccan).

Bright white deposits of chromium were obtained from potassium dichromate baths, containing sulphuric acid or potassium hydrogen sulphate. Baths containing potassium sulphate yielded grey deposits. The current efficiency in the case of sulphuric acid was about 9% and in the case of potassium hydrogen sulphate about 5%. It was very low in the case of potassium sulphate.

10. Electro-deposition of chromium from potassium dichromate baths. Part II: In presence of acetate.

S. R. PATHAK and S. HUSAIN, Hyderabad (Deccan).

Shining white deposits of chromium were obtained from potassium dichromate baths containing acetic acid or sodium acetate. The current efficiency in the case of acetic acid baths was about 14% and in the case of sodium acetate it was about 0.6% only.

11. Investigations on hyponitritosulphates.

N. V. DHAKAN and C. C. SHAH, Baroda.

Pure potassium hyponitritosulphate has been successfully prepared and its reactions studied. The following equations represent the course of its spontaneous decomposition:—



The course of the reaction depends on the concentration, temperature and the  $p_{\text{H}}$  value of the solution. In ordinary air, the solid salt decomposes, mainly according to equation (1). Anhydrous carbon dioxide has no effect upon the salt. In saturated water vapour, the salt decomposes rapidly into sulphate and nitrous oxide. The aqueous solution of the salt is unstable and decomposes according to equation (1). All kinds of acids decompose the salt in accordance with equation (1), but alkalies appear to have a stabilizing influence.

In acidic solution, potassium hyponitritosulphate is neither oxidized by the commoner oxidizing agents, such as potassium permanganate, iodine, bromine, sodium bromate, hypoiodite, hypobromite, etc., nor reduced by stannous chloride and hydrochloric acid, stannous chloride and titanous chloride, sodium bisulphite and hydrochloric acid, zinc, and acetic acid, etc.

In alkaline solution, potassium permanganate and sodium hypochlorite oxidize it with the formation of potassium sulphate and nitric acid; all the nitrogen does not, however, get converted into nitric acid, some of it escaping as nitrous oxide.

By the action of alkaline reducing agents a very small amount of ammonia is formed, and products, such as hydrazine, potassium sulphite, sulphate, etc., are detected. The results obtained so far show that the hyponitritosulphuric acid probably exists in two forms  $\text{KO} \cdot \text{SO}_2\text{NO}$ :  $\text{N} \cdot \text{OK}$  (1) and  $\text{KSO}_3 \cdot \text{N} \cdot \text{O} \cdot \text{N} \cdot \text{OK}$  (2).

Sodium and ammonium hyponitritosulphates and the double salts of zinc, cobalt, manganese, cadmium, silver, and barium have been prepared, and their chemical properties are being examined.

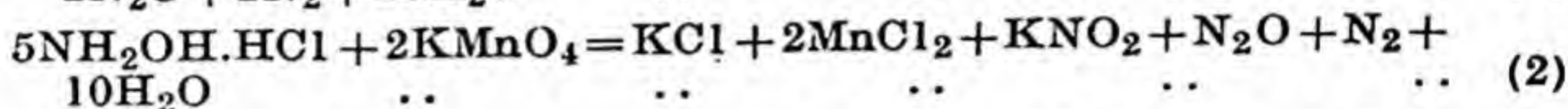
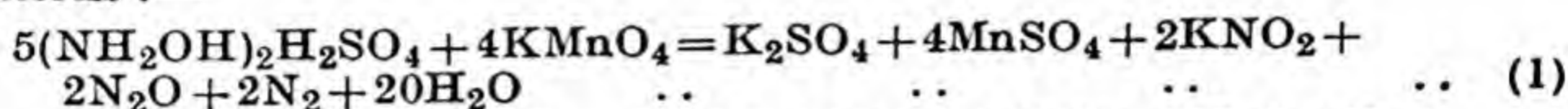


## 12. Oxidation of hydroxylamine sulphate and hydrochloride by means of potassium permanganate.

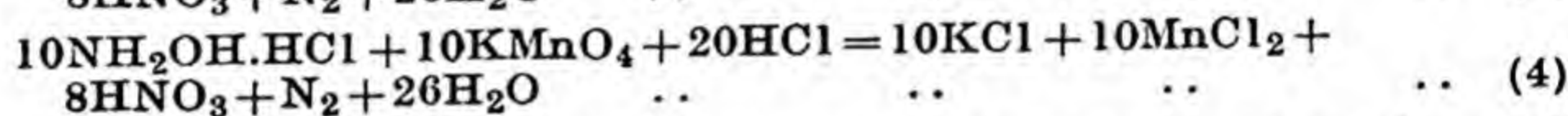
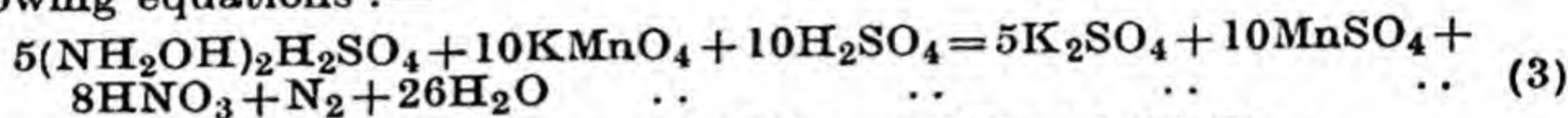
N. V. DHAKAN and C. C. SHAH, Baroda.

In the reduction of nitric acid to ammonia, hyponitrous acid has been considered as an intermediate product (*J. Phys. Chem.*, 1926, 30, 1222). But it has been shown by Partington and Shah (*J. Chem. Soc.*, 1931, p. 2071), that hyponitrous acid cannot be reduced to ammonia though it can be oxidized to nitric acid to a certain extent. Leaving out nitrogen, hydroxylamine should be the first reduction product of hyponitrous acid. In order to elucidate this behaviour, experiments have been conducted to study the oxidation of hydroxylamine by potassium permanganate.

The course of the oxidation of hydroxylamine by potassium permanganate in neutral solution can be represented by the following equations:—



In acidic solution, the course of oxidation is represented by the following equations:—



The course of the oxidation is dependent on the concentration and the  $\text{pH}$  value of the solution, temperature having little effect.

It appears from the results so far obtained that the velocity of the oxidation reaction is very small. Further work is in progress.

## 13. Formation and properties of polyiodides.

M. D. AVASARE and A. M. TRIVEDI, Baroda.

Phase rule study of the system  $\text{NH}_4\text{I}-\text{I}_2-\text{CCl}_4$  at  $30^\circ$  showed the formation of a binary compound  $\text{NH}_4\text{I}_3$ , as confirmed by quantitative examination and by measurement of its dissociation pressure.

Treatment of an aqueous solution of ammonium iodide of definite concentration results in the formation of  $\text{NH}_4\text{I}_5$ —a very hygroscopic and unstable compound.

A detailed study of the solubility of iodine in aqueous solutions of (1) sodium, (2) potassium, and (3) ammonium iodides has shown the formation of (a)  $\text{NaI}_3$ ,  $\text{KI}_3$  and  $\text{NH}_4\text{I}_3$  only when the salt solutions of concentration range 0.017 M to 0.7 M were used, and (b) the formation of  $\text{NaI}_5$ ,  $\text{KI}_5$  and  $\text{NH}_4\text{I}_5$ , and  $\text{NaI}_7$ ,  $\text{KI}_7$  and  $\text{NH}_4\text{I}_7$  when the salt concentrations above 1 molar to saturation were employed.

## 14. Study on the alkaline Nessler's reagent.

P. B. SARKAR and B. C. RAY, Calcutta.

Neutral Nessler's reagent does not give characteristic precipitate with free ammonia. The presence of caustic alkali is indispensable. In ordinary text-books the roll of  $\text{OH}'$  ion is not properly taken consideration of. Physico-chemical methods have been applied to study the behaviour of  $\text{HgI}_4'$  ion in presence of  $\text{OH}'$  ion.



15. The metallic constituents of certain Indian foods and vegetables : complete quantitative analysis (chemical and spectrographical).

P. B. SARKAR and H. C. GOSWAMI, Calcutta.

The present paper forms the first communication of a systematic examination of all the metallic constituents present in Indian vegetables. The following species have been analyzed :

Atap rice ; *Musa sapientum* ; *Momordica charantia* (bitter variety) ; *Trichosanthes dioica* ; *Piper betle*. All of them contain the following metals per kg. :—

Cu, 0.5 to 2.5 mg. ; Mo, 0.03 mg. ; Fe, 1.4 to 31.17 mg. ; Al, 21.6 mg. ; Zn, 1.2 to 2.4 mg. ; Mn, 0.12 to 3.5 mg. ; CaO, 245 to 984 mg. ; MgO, 250 to 669 mg. ; Na<sub>2</sub>O, 377 mg. ; K<sub>2</sub>O, 4900 mg.

16. Inorganic constituents of Indian vegetables.

K. KONDAIAH, Benares.

A systematic analysis of a large variety of Indian vegetables, for their inorganic constituents, has been undertaken. The materials are first dried and then ashed in platinum. The ash is then analyzed according to standard methods. The constituents estimated include iron, manganese, phosphorus, alkalis, and silica. Manganese, iron, and phosphorus have so far been estimated in the following vegetables : soya sag, palak sag, bathua sag, bendi, bohada, sem, bigan, paravar, nenua, lauki, kohada. When the data of the analyses are complete, an effort will be made to study the influence of these inorganic constituents on nutrition.

17. On the formation of complexes between manganic fluoride and potassium fluoride.

R. C. RAY and H. C. MITRA, Patna.

The formation of complexes between manganic and potassium fluorides has been investigated. It has been found that only two complexes of the formulæ  $MnF_3.KF$  and  $MnF_3.2KF$  are formed.

18. A method of qualitative analysis without the use of hydrogen sulphide.

M. R. RANE and K. KONDAIAH, Benares.

This scheme of qualitative analysis of the common basic radicals, which dispenses with the use of hydrogen sulphide, is simple, expeditious and accurate. The bases are separated into five main groups. The first group (A) consists of silver chloride and the insoluble oxides of antimony and tin, formed by hydrochloric and nitric acids. The second group (B) includes barium, strontium, and lead, which are precipitated as sulphates by ammonium sulphate in acid medium. The third group (C) consists of iron, aluminium, chromium, manganese, bismuth, calcium, and magnesium, which do not form soluble ammoniacal complexes with ammonia and are precipitated by ammonia and ammonium phosphate. Cobalt, nickel, copper, cadmium, and mercury, which are precipitated as oxides or hydrated oxides, when their ammoniacal complexes are boiled with sodium hydroxide are included in the fourth group (D) while zinc and arsenic remaining in solution to the end constitute the fifth group (E). Alkalis and ammonium are tested for separately in the original mixture.



## PHYSICAL CHEMISTRY.

19. On the photo-bromination of acetylene dichloride in the gaseous phase and in carbon tetrachloride solution.

J. C. GHOSH, S. K. BHATTACHARYYA, and S. C. BHATTACHARYYA, Dacca.

The photo-bromination of acetylene dichloride in the carbon tetrachloride solution has been done in three different frequencies, 406, 436, and 546  $\mu\mu$ . The reaction is unimolecular with respect to bromine. The reaction was carried out at 30°C. At this temperature there is no dark reaction between the components of the reaction mixture. This reaction has got the following characteristics :—

(a) The unimolecular velocity constant with respect to bromine diminishes slightly with time.

(b) The velocity constant diminishes with diminishing concentration of the acetylene dichloride when the concentration of the latter is below  $\cdot 0054M$ , according to the relation  $1/K$  plotted against  $1/C$  gives a straight line. When the concentration of the acceptor exceeds  $\cdot 0054M$ , the velocity constant is practically independent of the concentration of the acceptor.

(c) Temperature coefficient is 1.4 for 546  $\mu\mu$ ; 1.38 for 436  $\mu\mu$ ; and 1.35 for 406  $\mu\mu$ .

(d)  $\gamma$  is equal to 2 for 546  $\mu\mu$ ; 6 for 436  $\mu\mu$ ; and 9 for 406  $\mu\mu$ .

A mechanism has been suggested to explain the above facts.

The photo-bromination of acetylene dichloride in the gaseous phase has been done in 436  $\mu\mu$  at 30°C. There is no dark reaction at this temperature. The mechanism of the gaseous reaction has been found to be identical with that of the reaction in  $CCl_4$  solution. Only the quantum efficiency  $\gamma$  has been found to be a little higher in the gaseous phase.

20. Effect of the simultaneous action of radiations of different frequencies on the photochemical oxidation of mandelic acid by bromine.

J. C. GHOSH and S. K. BHATTACHARYYA, Dacca.

The kinetics of the reaction were first separately studied in three monochromatic radiations 366, 436, and 546  $\mu\mu$  and then, under the simultaneous action of the ultraviolet (366  $\mu\mu$ ) and the blue (436  $\mu\mu$ ); the ultraviolet (366  $\mu\mu$ ) and the green (546  $\mu\mu$ ) and the blue (436  $\mu\mu$ ) and the green (546  $\mu\mu$ ) radiations. The reaction is zero-molecular with respect to bromine in presence of potassium bromide. The bromination was carried out at 31.5°C. At this temperature there is a slight unimolecular dark reaction between the components of the reaction mixture. The reactions were studied in two different concentrations of bromine and bromide, the composition of the reaction mixture being those used by Ghosh and Purkayastha (Z. Physik. Chem. Abt. B. Bd 7, Heft 4, 285, 1929).

The results obtained are peculiar in the following respects :—

(a) The combined effect of two radiations is always less than the sum of the two individual effects.

(b) The velocity constant in pure monochromatic radiation varies as the square root of the intensity of the absorbed radiation.

(c)  $\gamma$  for 366  $\mu\mu$  varies from 25 to 100; for 436  $\mu\mu$  varies from 13 to 57; and for 546  $\mu\mu$  varies from 3 to 12.

A mechanism has been given to account for the above observed peculiarities.



## 21. The photo-expansion in chlorine.

T. S. NARAYANA, Waltair.

Experiments were carried out on the influence of temperature on the photo-expansion of chlorine. It was found to be independent of temperature; and this result has definitely thrown light on the mechanism of the Budde Effect in halogens. It was therefore concluded that the photo-expansion is entirely due to the mechanism put forward in a previous communication (*Ind. Journ. Phys.*, Vol. IX, part II, 1934) and not due to the thermal changes brought about by collision of activated molecules.

## 22. Effect of ultraviolet light on ferric salts of organic acids.

P. B. GANGULI and PANNALAL, Patna.

Ferric salts of citric, tartaric, salicylic, and malonic acids were prepared from freshly precipitated ferric hydroxide and exposed to ultraviolet light. The rate of reduction was followed by Mohr's iodometric method (*Ann. d. Chem. U. Pharm.*, 105, 53). The order of the reactions has been found to be mono-molecular. In a quartz vessel the reaction is much more rapid than in a glass vessel (cf. *Benrath. Zeit. phys. Chem.*, 74, 150, 1910). This is not a surface effect, as addition of silica gel has a slight retarding influence. Light of wavelength greater than 4850 Å units is inoperative. The effects of traces of copper, uranium, and thorium have been investigated.

Freshly precipitated ferric hydroxide dissolves in stoichiometric quantities of the organic acids to form in the beginning a colloidal solution, which gradually passes over to a crystalloidal form. This has been followed by dialysis and estimation of the dialysate.

23. Raman spectra of *cis* and *trans* decalins.

S. K. KULKARNI JATKAR, Bangalore.

In continuation of previous work the shifts 539 (0), 595 (3), 794 (1), 1040 (2), 1270 (5), 1347 (3b) have been found to be characteristic of *cis* and 495 (5), 881 (3), 957 (1), 996 (2), 1145 (3), 1234 (1), 1363 (5b) are characteristic of *trans* decalin. A comparison of these observations with the Raman spectra of *cis* and *trans* ortho dimethyl cyclohexane shows that the *cis* and *trans* positions in these compounds are similarly configured to that of *cis* and *trans* decalin, and brings out the persistence of group frequencies in increasingly complex compounds.

24. Raman spectra of  $\alpha$  and  $\beta$  picolines, quinoline, quinaldine, and isoquinoline.

S. K. KULKARNI JATKAR, Bangalore.

Evidence has been found in the Raman spectra in support of the peculiar and characteristic properties of these compounds, such as the dual nature of the stability of the constituent rings when compared with naphthalene and the reactivity of the methyl group.

The occurrence of paired lines at 500, 1000, 1278, 1430, and 1550  $\text{Cm}^{-1}$  in isoquinoline indicate the existence of two forms of this compound, one having a quinoline structure and other quinaldine structure.

## 25. Raman spectra of terpenes and camphors.

S. K. KULKARNI JATKAR and R. PADMANABHAN, Bangalore.

The marked differences in the Raman spectra of limonene and dipentene have been shown to be due to the different amounts of the products of intramolecular isomerization namely, terpinolene and  $\alpha$



terpinene present in these compounds, the latter predominating in the technical dipentene.

There are three faint shifts 1412 (1), 1440 (1) and 1480 (0)  $\text{Cm}^{-1}$  in camphor, and only two lines 1450 (5) and 1484 (2) in fenchone, the smaller value and lower intensity of the band in camphor being due to the reactive nature of the methylene group.

26. On the formation of liesegang rings in the presence of precipitates. Part I: Action of potassium ferrocyanide on ferric chloride in presence of calcium sulphate and barium sulphate precipitates.

B. N. SEN, Calcutta.

Known volumes of the solution of potassium ferrocyanide were kept over thickly set bodies of the precipitates of calcium sulphate and barium sulphate prepared by moistening given weights of these precipitates with ferric chloride solution. It was found that the Prussian blue precipitates appeared in the form of periodic rings in the uniformly set bodies of these precipitates. The number, the thickness of and the distance between the rings have been studied with reference to the concentration of the reactants, acidity of the medium and to other factors which generally influence the characteristics of the rings.

27. On the formation of liesegang rings in presence of precipitates. Part II: Action of potassium ferrocyanide on copper sulphate in presence of calcium sulphate and barium sulphate precipitates.

B. N. SEN, Calcutta.

Uniformly set bodies of the precipitates of calcium sulphate and barium sulphate were prepared by moistening given weights of these precipitates with copper sulphate solution. Known volumes of potassium ferrocyanide solution were kept over these bodies, when it was found that the copper ferrocyanide precipitate appeared in the form of periodic bands in the uniformly set bodies of these precipitates. The characteristics of the bands have been studied with reference to the concentration of the reactants and the acidity of the medium.

28. Effect of lyophillic colloids on the wettability of naphthalene by water.

A. C. CHATTERJI, Lucknow.

It has been pointed out by J. Traube (*Chemikar Ztg.*, 1924, 48, 633, 673) that the addition of minute quantities of lyophillic colloids considerably influences the wettability of ores when a separation of these is attempted by the flotation process. In a number of former papers (*Kolloid Beiheften*, 10/12 Band 38, 1933; *Proc. Ind. Sc. Cong.*, 1934) it has been pointed out that there exists a close relation between capillary activity and wettability, and further the wettability of pure chemicals like naphthalene, anthracene, and phenanthrene, are also considerably affected by capillary active substance.

In this paper the effect of adding minute quantities of some lyophillic colloids on the wettability of naphthalene has been studied. The colloids examined are gelatin, casein, starch, agar-agar, and silicic acid.

The method employed for the determination of wettability is the one described in *Kolloid-Beihefte*. According to the results obtained the colloids can be arranged in the following order:—

gelatin > casein > starch : agar-agar > silicic acid.



It is interesting to compare this series with that obtained on a basis of their gold numbers,—

gelatin > casein > starch > silicic acid.

29. The anomalous coagulative power of mercury chloride.

S. S. JOSHI and K. R. DAS, Benares.

In a communication to be published shortly in *J. Indian Chem. Soc.*, results are presented to show that during the slow coagulation of colloid arsenious sulphide by aqueous solutions of mercury chloride, the variation of the viscosity, the transparency and the refractive index is abnormal. Systematic determinations were, therefore, made of the coagulative power (relative) of the above substance in the case of a number of colloids. This quantity was found to be abnormally high, and has been discussed especially in view of the fact that aqueous solutions of mercury chloride show but negligible ionization, as judged by conductivity and other allied data.

30. Influence of high temperature ageing on the refractivity of colloids.

S. S. JOSHI and P. V. JAGANNATH RAO, Benares.

This was undertaken in order to investigate the general nature of factors which determine the refractive index of a colloidal solution.

To this end, variously concentrated colloidal solutions of manganese dioxide, antimony sulphide, arsenious sulphide, cupric oxide, sulphur, vanadic acid, aluminium hydroxide, selenium, silver, cadmium sulphide, prussian blue, copper ferrocyanide, mercuric sulphide, gold, ferric hydroxide, and some oil emulsions were held at 100°C. about 3.5 hours, under reflux condenser and at constant colloid content. In all these systems, except with aluminium hydroxide, the refractivity was found to increase by subjecting the sol to heat as mentioned above, and the change in the refractive index was independent of the nature of the colloid.

31. Coagulation of colloid manganese dioxide in the slow region.

S. S. JOSHI and P. V. JAGANNATH RAO, Benares.

Kinetics of the slow coagulation of colloid manganese dioxide has been studied in the presence of various amounts of potassium, barium, mercury and aluminium chlorides, and lanthanum and thorium nitrate. The course of coagulation was followed by measurement of the viscosity and the refractive index of the coagulating sol. In agreement with previous results with a number of other sols whose coagulation kinetics have been studied in these laboratories (Joshi and collaborators, *J. Indian Chem. Soc.*, 1933, 10, 329; 1933, 10, 599; 1934, 11, 133; 1934, 11, 555-571; 572-577; 1934, 11, 797-804; *J. Chem. Phys.*, 1935, 3, 455) it was found that coagulation in the slow regions showed usually an initial viscosity diminution and a discontinuous variation. The use of the refractive index to follow the course of coagulations, developed first in these laboratories, has provided curves of striking simplicity, the discontinuities being spaced unambiguously and well distributed in the coagulation time.

32. The effect of light on some colloids.

P. N. RAO and M. QURESHI, Hyderabad.

A number of sols were exposed to ultraviolet light. In the majority of cases the  $P_H$  values of the systems before and after illumination were



determined. In the case of the ferric hydroxide sol, the  $P_H$  values as well as the extinction coefficients of the system before and after illumination for different periods of time were determined. In the case of arsenious sulphide, mercuric sulphide, mastic and gamboge sols the  $P_H$  value decreases on exposure to light. With ferric hydroxide sol the  $P_H$  values and extinction coefficients both show a decrease on shorter exposures. But prolonged exposures lead to an increase in both the  $P_H$  values as well as the extinction coefficients. An explanation for the changes observed in the  $P_H$  values and the extinction coefficients of the ferric hydroxide sol has been offered. The effect of ageing on the  $P_H$  value of the ferric hydroxide sol is in the same direction as that of the ultraviolet light.

### 33. Specific heat of colloidal solutions.

S. S. JOSHI and G. R. PHANSALKAR, Benares.

A review of the rapidly growing and already very considerable literature on the physical properties of colloids shows the absence of any quantitative data on the heat capacity of these systems. This information is, however, of fundamental importance in the elucidation of the well-known effects of temperature on the different aspects of colloidal behaviour; and as such it is of more than theoretical significance, e.g., in the case of soil colloids. A beginning has therefore been made in this line in these laboratories in the determinations of the specific heats of colloidal solutions of arsenious sulphide, antimony sulphide, manganese dioxide, gamboge, and gum-dammar by using an adiabatic calorimeter with an accuracy of at least 12 in 10,000. The specific heat of arsenious sulphide, manganese dioxide, and gum-dammar is found to be less, and that of gamboge to be greater than that of water. The specific heat of antimony sulphide when fresh is greater than that of water; it decreases with ageing and finally falls to a value less than that of water. A similar effect on the specific heat of arsenious sulphide is also found.

### 34. Studies on desorptions of vapours in silica gel.

R. C. RAY and P. B. GANGULY, Patna.

In continuation of the previous work on the adsorption of water vapour by silica gel (*Trans. Faraday. Soc.*, 1934), the desorption of vapours of water, alcohol, and benzene has been determined. The phenomenon of hysteresis has been discussed in the light of the formation of loose adsorption compounds.

### 35. The velocity of sound in air and steam in narrow tubes.

S. K. KULKARNI JATKAR, Bangalore.

The velocity of sound in air has been determined in smooth brass tubes of 9.5 mm. and 5.5 mm. diameter at frequencies 23586, 49460, 94500 and 127000 cycles and at 25°, 97.1°, and 134°. The effect of these factors on the Helmholtz Kirchhoff constant is to increase the values at higher temperatures. The corrected values for velocity of air in meters per sec. are 345.7 at 24°, 387.4 at 97.1°, and 399.2 at 134°. For steam the uncorrected values are 493.3 at 94 k.c. and 494.3 at 127 k.c. in a tube of 5.5 mm. diameter.

### 36. The velocity of sound in organic vapours.

S. K. KULKARNI JATKAR, Bangalore.

Continuing previous work (*Proc. Ind. Science Congress*, Bombay, 1934), the following values of the velocity of sound have been obtained



at 134°, at 94 and 127 k.c. in a brass tube 5.5 mm. in diameter. The values for two frequencies are :

Temperature 134°.		
	94 k.c.	127 k.c.
CH <sub>3</sub> OH ..	352.9	352.8
EtOH ..	284.3	284.4
nPrOH ..	250.7	..
<i>Tert</i> -BuOH ..	226.3	..
(CH <sub>3</sub> ) <sub>2</sub> CO ..	251.1	251.2
Et <sub>2</sub> O ..	217.4	217.5
Ethyl acetate ..	195.3	..
CH <sub>2</sub> Cl <sub>2</sub> ..	210.6	..
CHCl <sub>3</sub> ..	179.5	178.1
CCl <sub>4</sub> ..	153.6	153.3
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> ..	190.1	190.6
C <sub>6</sub> H <sub>6</sub> ..	212.7	212.8
C <sub>6</sub> H <sub>12</sub> ..	202.1	201.7
nC <sub>6</sub> H <sub>14</sub> ..	199.5	207.3 ?

### 37. The free energy of organic compounds.

S. K. KULKARNI JATKAR, Bangalore.

Using the values of equilibrium constants obtained by the author and co-workers, the free energy of formation of methyl ether, ethyl ether, *n*-propyl ether, methyl acetate, ethyl acetate, and propyl acetate have been calculated, and the need for further work in this line is emphasized in this paper.

### 38. The corona pressure phenomenon in gases under electrical discharges due to fields of low frequency.

S. S. JOSHI and A. J. HARI RAO, Benares.

It was observed that when elementary gases like nitrogen, hydrogen, and oxygen were subjected to ionization by collision in the annular space of Siemen's tubes, an instantaneous pressure rise of about 2 cm. Hg, followed by a slower pressure change was observed. The influence of initial pressure, applied voltage, the ionization current, frequency of the applied field, capacity (electrical) of the annular space, the type of the discharge, on the magnitude of the initial or the corona pressure change has been investigated. Detailed results are obtained for the actual temperatures of the gas under varying conditions of the discharge. These data, and the fact that the initial pressure rise is independent of the rate of electrode cooling, militate against the adoption of an entirely thermal origin for the initial pressure change. The influence of ozone on the corona pressure rise has been found in general to depress it.

### 39. The decomposition of nitric oxide in electric discharge due to alternating fields of low frequency.

S. S. JOSHI and K. S. VISVANATH, Benares.

The discharge tube was essentially similar to the familiar Siemen's ozoniser, in the annular space of which the gas was exposed to ionization by collision. The potential applied was increased up to about 5,000 volts (r.m.s.). The gas pressure was varied in the range 2.0 to 31.5 cm. Hg. At constant applied voltage, duration of the reaction increased markedly with the gas pressure in a manner not unlike that observed in the case of zero-molecular reactions. Determinations of the ionization



current at different times during the decomposition, and of the gas pressure at constant volume, reveal a striking similarity between the current-time and the pressure-time curves. An intermediate formation of nitrogen peroxide is definitely established. The final products are nitrogen and oxygen in the ratio 1:1. The current flowing through the reaction vessel is very markedly affected by the production of nitrogen peroxide. Results are given for the analysis of the decomposition mixtures at different stages of the reaction and also for mixtures analyzed after constant intervals of exposure to discharge at different initial pressures. It has been found that increase of the gas pressure diminishes the velocity of the reaction at constant applied potential. This finding has been discussed from the standpoint of the law of Mass Action and other theories of the phenomenon (Elliot, Josh and Lunt, *Trans. Faraday Soc.*, 1927, 23, 57).

#### 40. Esterification equilibria in vapour phase.

S. K. KULKARNI JATKAR and N. G. GAJENDRAGAD, Bangalore.

Continuing the previous work with silica gel as the catalyst, the following final values have been obtained for the percentage conversion of the equimolecular mixtures of both ethyl and methyl alcohols with acetic acid, viz. 78.5% and 75% at 230° and 250° respectively. The high temperature coefficient is in harmony with the results of Clark and Essex in the range 150°–200°, the importance of our results lying in the fact that the corrections for the association of acetic acid and compressibilities are negligible in the range of temperatures we have tried. The results of all workers have been correlated in this paper.

#### 41. The system methyl-ether-sulphuric acid and *n*-propyl-ether-sulphuric acid.

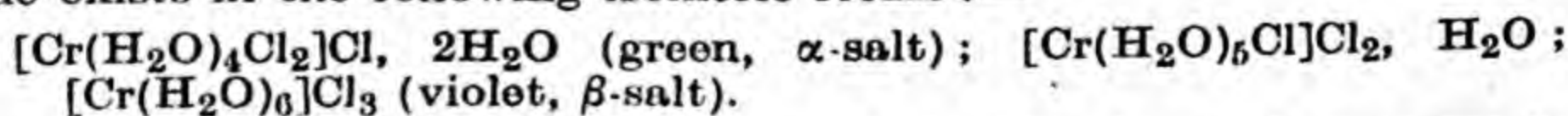
S. K. KULKARNI JATKAR and N. G. GAJENDRAGAD, Bangalore.

Although the system sulphuric acid ethyl ether has been studied by Pound (1921) and recently by Usanovich (1934), the study of the systems of sulphuric acid with other ethers has not been reported so far. The authors have recorded the values of conductivity and viscosity of the system sulphuric acid-methyl ether and sulphuric acid-propyl ether. With increasing addition of methyl ether the viscosity drops sharply and remains constant, and again increases rapidly when the molar composition of 50 per cent. is reached. In the case of *n*-propyl ether after the initial drop the viscosity attains a maximum which is one and half times that of pure sulphuric acid, at 50 per cent. molar composition. The maximum conductivity when corrected for viscosity shows a maximum at 94 per cent. of sulphuric acid in both methyl and propyl ethers. The results are compared with the corresponding properties of the system  $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4-\text{Et}_2\text{O}$ .

#### 42. Colour transformation in aqueous solutions of chromium chloride.

S. S. JOSHI and K. P. N. PANNIKAR, Benares.

It is considered (Meunier and Les Bre, *Compt. rend.*, 1930, 190, 183–185; Partington and Tweedy, *Nature*, 1926, 117, 415) that chromium chloride exists in the following isomeric forms:—



An exhaustive study of the conditions, and the kinetics of these isomeric transformations has been made by measurements of (a) electrical conductivity, (b) absorption spectra, (c) refractive index, and (d) viscosity.



Results are also given for the influence of exposure to short wave radiations and of temperature in the catalysis of the above changes.

43. A study of the nature of the copper-ammonia complex solutions.

S. S. JOSHI and K. VYASULU, Benares.

A study has been made of the nature and constitution of copper-ammonia complexes existing in aqueous solution and similarly coloured solutions obtained by peptizing cupric hydroxide with excess of alkali and organic hydroxy compounds like glycerol, glucose, sucrose, Roschelle salt, etc. Copper ammonia complex solution has been prepared by dissolution of metallic copper in ammonia by the air bubbling process, and by adding ammonia to copper salts. The absorption spectra of these solutions are found to be similar, but colorimetric observations disclosed interesting differences. The depth of light absorption was found to be greater with copper-ammonia solutions than with other systems. Cataphoreses and dialysis experiments indicated the presence of colloidal cupric hydroxide in every case.

The influence on the viscosity of the addition of varying amounts of ammonia to copper salts, cupric sulphate, cupric chloride, and cupric nitrate was also investigated. There was an initial fall in viscosity on the addition of four moles of ammonia to one mole of copper salt. Further addition of ammonia increased the viscosity almost linearly. Thus the viscosity-concentration curves indicated only one definite break corresponding to the addition of four moles of ammonia. The results are in agreement with those obtained by Blanchard in his investigations on the viscosity of the cuprammonium solutions. Results are also obtained for the variation of other physical properties, such as refractivity, in relation to the composition of the mixtures which is most favourable for the complex formation.

44. The dissociation constant of some acids by solubility measurements.

W. V. BHAGWAT, Indore.

Bhagwat and Dhar (*J. Indian Chem. Soc.*, 1929, 6, 807), Bhagwat and Doosaj (*ibid.*, 1933, 10, 477) have determined the dissociation constants of several acids by solubility measurements. They have also tried to determine the limit of application of this method. The work has been extended and the dissociation constants of benzene sulphonic acid, propionic acid, oleic acid, butyric acid, etc. have been determined. Further work as regards the limitations of this method to these acids is in progress.

45. The reaction between aqueous iodine and sodium formate, and the effect of various salts upon it.

W. V. BHAGWAT, Indore.

The reaction between sodium formate and iodine in the presence of potassium iodide has been investigated by Dhar (*J. Chem. Soc.*, 1917, 111, 707), Bhattacharya and Dhar (*J. Indian Chem. Soc.*, 1929, 6, 475), Bhagwat and Doosaj (*ibid.*, 1934, 11, 331; *Z. anorg. u. allg. Chem.*, 1934, 216, 241). The present work deals with aqueous iodine and the effect of such salts as potassium sulphate, potassium chloride, sodium nitrate, and others. The temperature coefficient in the dark for five degrees is 1.5 between 29 and 34, for aqueous iodine. Potassium sulphate, potassium and sodium nitrate retard the reaction. The results with the three chlorides—potassium, sodium, and ammonium chloride—show that the velocity



coefficient in all cases increases with the increase of the amount of the salts at first, and then falls when the concentrations are further increased. The value of the temperature coefficient in the presence of these salts is found to be governed by the value of the initial velocity.

46. The electronic theory and the stability of sextets.

P. B. SARKAR and B. C. RAY, Calcutta.

Its generalization in explaining the structure of simple ions, inorganic and organic—e.g. carbonate, nitrite, formate, etc. Detailed discussion specially regarding the structure of formate ion from chemical and physico-chemical data.

47. The kinetics of the benzoin reaction in the presence of solvents.

P. S. REGE and T. S. WHEELER, Bombay.

In continuation of the work described last year, the benzoin reaction has been studied in the presence of diluents, like chloroform, carbon tetrachloride, pentane, cyclohexane, benzene, toluene, and their chloro-derivatives. The rate of the homogeneous autocatalyzed reaction has been found to decrease with increase in the amount of the solvent. Benzyl chloride shows the greatest inhibiting effect. The inhibition can be explained on the assumption that the trace of the cyanide dissolved in benzaldehyde, which is responsible for the autocatalyzed reaction, is precipitated by the solvent. Assuming that the heterogeneous reaction on the surface of the solid cyanide is unaffected, it has been found that the time-yield curves obtained with the inert solvents admit of a kinetic interpretation. Acetone has been found to accelerate the rate of the homogeneous reaction.

The reaction has also been studied in the presence of methyl and ethyl alcohols, ethylene glycol, and glycerol. Small quantities of these alcohols gradually increase the rate of the reaction; larger ones delay the starting point of the accelerated reaction; whereas still larger quantities accelerate the reaction right from the beginning. Small quantities of polyhydric alcohols increase the rate of the reaction.

48. The thermal decomposition of mercurous nitrate.

M. S. SHAH and B. G. JOSHI, Amhedabad.

The decomposition of hydrated and anhydrous mercurous nitrate has been studied quantitatively by heating the substance *in vacuo* and analyzing the solid and gaseous products. The monohydrate loses water and then behaves like the anhydrous salt. The latter becomes pale yellow at about 45° and decomposes below 100° evolving nitrogen peroxide and leaving a yellow residue of the composition:  $\text{HgNO}_3, 2\text{HgO}$ . On further heating up to 200° no change occurs, but above 200°,  $\text{HgNO}_3, 2\text{HgO}$  loses nitrogen peroxide and is converted into mercuric oxide. At any stage during decomposition if the system be allowed to cool down all nitrogen peroxide is reabsorbed forming mercurous nitrate, thus showing that the change is reversible.

49. The thermal decomposition of 'spent acetate of lime'.

BALWANT SINGH, GURBACHAN SINGH, and H. B. DUNNICLIFF, Lahore.

It has been found that calcium carbonate in spent acetate of lime is completely decomposed into calcium oxide when heated for half an hour at 900°C. In a current of air, quantitative decomposition took



place at 700°C. to 720°C. and, in the presence of steam, at about 660°C. in the same interval of time. The spent acetate of lime, when heated at 650–700°C. mixed with 10% carbon, gave a quantitative yield of calcium oxide in 30 minutes. In a current of air and steam the calcium carbonate in the spent acetate mixed with carbon was decomposed completely at 600–620°C. in half an hour.

# 50. A potentiometric study of some oxidation-reduction reactions.

BALWANT SINGH, IJAZ ILAHI, and H. B. DUNNICLIFF, Lahore.

*Oxidation with potassium iodate:*—Potassium iodate has been used as an oxidizing agent in the potentiometric estimation of antimonite, arsenite, dichromate, permanganate, tetrathionate, in ferrous, stannous, mercurous, and thallos salts and in hydrazine sulphate by Andrew's method. The concentration of hydrochloric acid was kept between 4–5 N in these titrations.

*Oxidation with chloramine-T:*—Potassium iodide and sodium sulphite have been determined by titrating them potentiometrically against a standard solution of chloramine-T.

*Reduction with sodium sulphite:*—Sodium sulphite has been used as a reducing agent in acid solution in the presence of an excess of potassium iodide to determine iodine, potassium dichromate, potassium ferricyanide, hydrogen peroxide, and copper sulphate by the potentiometric method.

# 51. On active charcoal.

M. D. AVASARE and S. N. DAVE, Baroda.

It has been known that the activity of charcoal, as measured by the magnitude of adsorption, depends on its physical nature, the temperature and time of activation and on the nature of the gas in which it is activated. It has further been known that the magnitude of adsorption on any given quality of active charcoal depends on the physical and chemical nature of the adsorbate.

During a series of experiments undertaken to investigate the correlation between the various factors that influence the activity of charcoal, it is found that the magnitude of adsorption on the charcoal depends on the degree of evacuation to which the active charcoal is subjected previous to the study of adsorption.

Under ordinary conditions of evacuation, adsorption is increased owing to an increase in the pore diameter caused by a partial removal of the oxide film, but on intensive evacuation its activity decreases to a large extent. The presence of the oxide film, therefore, is essential for a high degree of activity.

# 52. The influence of sorbed oxygen and nitric oxide on the retention of carbon monoxide and sulphur dioxide by charcoal.

M. S. SHAH and S. G. SHARANGPANI, Ahmedabad.

The adsorption of carbon monoxide and sulphur dioxide has been studied at 0° on purified sugar charcoal (a) exhausted at 900°, (b) containing sorbed oxygen, and (c) containing sorbed oxygen and nitric oxide. From the results of analysis of the gases pumped off at 0° and on subsequent heat treatment of charcoal in vacuo to 170° and 900°, it is observed that with charcoal in (a) and (b) both carbon monoxide and sulphur dioxide are completely removed as such on desorption at 0° and at 0° and 170° respectively, while with charcoal in (c) the retention of a part of both these gases takes place. Carbon monoxide thus retained at 0° is evolved



in the form of carbon dioxide on raising the temperature to  $170^{\circ}$ , whereas sulphur dioxide is given out along with the gas coming off at  $900^{\circ}$ . It appears that both carbon monoxide and sulphur dioxide thus retained are oxidized, by sorbed oxygen and nitric oxide on the surface of charcoal, to carbon dioxide and sulphur trioxide respectively. The former is evolved as such, while the latter gets reduced by charcoal when the temperature is raised and hence is found as sulphur dioxide.

53. Heats of adsorption of nitric oxide on charcoal (a) exhausted at  $900^{\circ}$ , (b) containing sorbed oxygen, and (c) containing sorbed oxygen and nitric oxide.

M. S. SHAH and S. G. SHARANGPANI, Ahmedabad.

In continuation of the previous work (*Proc. Ind. Sc. Cong.*, 1934, p. 211) the authors have conducted experiments for the accurate measurements of—

- (I) the heats evolved during the adsorption of nitric oxide at  $0^{\circ}$  and 1 A.P. for a period of 24 hours on purified sugar charcoal (a) exhausted at  $900^{\circ}$ , (b) containing sorbed oxygen derived from nitric oxide treatment in (a) followed by evacuation at  $170^{\circ}$ , and (c) containing sorbed oxygen and nitric oxide derived from the system in (a) on evacuation at  $0^{\circ}$ , and
- (II) the heats absorbed during the desorption of each of the systems (a), (b), and (c) in (I).

From the analytical results of the gases pumped off at  $0^{\circ}$  and the values of the heats absorbed during desorption in (II), together with the fact that carbon dioxide and nitrogen are completely desorbed from the system at  $0^{\circ}$  (Shah and Sharangpani, *loc. cit.*), the heats of adsorption of nitric oxide per gram molecule on the surface of charcoal in (a), (b), and (c) are calculated and found to be 7513, 9605, and 1773 calories respectively.

54. The kinetics of the reaction between chloral hydrate and sodium hydroxide in dilute aqueous solutions.

A. N. KAPPANNA, Nagpur.

A detailed study of the kinetics of the reaction has been made. The biomolecular velocity constant varies with the initial concentrations of the reactants. A reaction mechanism which accounts for the observed results has been suggested.

55. On the effect of addition of mineral acids on the surface tensions of soap solutions.

A. NAGARAJA RAO, Bangalore.

The influence of different salts on the detergent properties of soaps has already been investigated by different workers, and the detergent action of soaps has been explained as being due to the lowered surface tensions of soap solutions when compared to water, which makes it possible for the dirt to get into the foam exactly as in the flotation process of ore concentration. The liberation of small quantities of the  $\text{OH}'$  by the hydrolysis of the soaps ( $\text{pH}$  thereby getting higher than 7) is also explained to exert its own influence in the detergent action.

The addition of mineral acids, by pushing back the hydrolysis of soaps and by suitably varying the  $\text{Ph}$  value of the medium, exerts its definite influence in the variation of the detergent action, which is here measured by the variation of the surface tensions of soap solutions with



the nature and concentration of the soap, and the nature and concentration of the mineral acid added.

56. Surface tension of aqueous solutions of electrolytes.

M. D. AVASARE and S. M. GAYWALA, Baroda.

Under a constant condition of temperature, the surface tension of aqueous solutions of salts is found to be greater than that of water. The temperature coefficient of the surface tension of water is constant over a wide range of temperature. It may be inferred, therefore, that the dissociation of the complex water molecules has no particular effect on surface tension. The principal factors affecting the surface tension of aqueous solutions may be, therefore, (1) ionic attraction and (2) hydration of ions.

Ionic attraction, a function of the electric charge, depends on the volume of the ion in the case of univalent ions, as the amount of charge is the same on each ion. If, in addition to an ion's comparatively greater radius, hydration occurs, the effect will be to increase the volume of the ion which effects a decrease in the surface density of the charge. Electrical attraction, therefore, diminishes, and consequently the value of the surface tension is found to increase. In the case of ions having smaller ionic radii and less hydration the increase in the value of surface tension is observed to be small. Hence it is concluded that ionic attraction, the value of which partly depends on the degree of hydration, directly affects surface tension.

Increase in the value of surface tension, over a considerable range of concentration, is found to be approximately a linear function of salt concentration, and may be expressed as :

$$\gamma_{s_1} - \gamma_{s_0} = km$$

where  $\gamma_{s_1}$  and  $\gamma_{s_0}$  stand for the surface tension of the solution and the solvent respectively,  $m$ , the number of gram-moles of the salt per litre, and  $k$  a constant.

57. The conductivity of pure soaps in ethyl alcohol and ethyl alcohol-water mixtures.

B. S. V. K. VITTAL and S. K. K. JATKAR, Bangalore.

Continuing the previous work (*Proc. Ind. Sci. Con.*, Allahabad, 1930), the study of the conductivity of soaps in alcohol-water mixtures has revealed the marked influence of the addition of small amounts of water. The solutions exhibited a minimum depending upon the dilution, Walden's rule being approximately obeyed. The effect of viscosity and dielectric constants of the solvent cannot quantitatively account for the results observed. The plot of conductivity against all suggested methods of calculations always exhibits a maxima or minima, and in some solutions both, although at higher concentrations they all yield flat straight lines. The behaviour observed is in agreement with the idea that in alcohol-water mixtures soaps behave as weak electrolytes.

58. The conductivity of benzoic acid in the presence of some chlorides in aqueous solutions.

S. S. JOSHI and D. N. SOLANKI, Benares.

The problem arose through finding in these laboratories that the partition coefficient,  $C_w/C_T$  (where  $C_w$  and  $C_T$  denote respectively the concentration of benzoic acid distributed between water and the toluene phase) usually diminished due to additions of electrolytes to the aqueous



phase. Determinations were therefore made of the influence on the conductivity of benzoic acid solution on adding varying amounts of the chlorides of lithium, sodium, potassium, rubidium and caesium, barium, mercury, and hydrochloric acid. The concentration of benzoic acid in each case was varied in the range  $N/4$  to  $N/400$ . Except in the case of hydrochloric acid, the specific conductivities of the mixtures, especially for low proportions of the solute, were in excellent agreement with the mixture law. The possibility of the variation of the activity of the undissociated benzoic acid due to addition of the above substances is investigated.

### 59. Hydration in aqueous solutions of electrolytes.

M. D. AVASARE and S. M. GAYWALA, Baroda.

It has been pointed out that hydration of ions contributes to a certain extent to the increase of viscosity of solutions, and that the dissociation of the complex water molecules alone supplies a rational proof of the observed phenomena of negative viscosity.

When the hydration of the kation is small and the non-hydrated anion is efficient in dissociating the complex molecules of the solvent to the extent that its effect on the lowering of viscosity predominates, the viscosity of the solution is negative. When the concentration of the salt solution is increased, the effect of the anion in bringing about dissociation of the complex water molecules is increased, and thus the average size of the water molecule is brought to its normal value. Under these circumstances the tendency of the hydrated kation to increase the viscosity of the solution becomes marked. It also accounts for the minimum value and subsequent increase of viscosity.

Sudgen has observed that hydration is independent of the concentration of the salt in solution. Results in this investigation, however, bear out that at concentrations ranging from 1 to 4 molar the hydration goes on falling with increase of concentration. This is evidently caused by the increased number of kations and anions in solution. It has been observed that the effect of kations and anions on hydration is opposite. Experimental evidence indicates that the effect of the anions predominates in solution.

It appears that there is a constant difference between the values of hydration for chlorides and nitrates of any given kation. The difference between the molecular hydration salts of any given set of alkali metals appears to be constant irrespective of the negative radical. It has thus been found that the kations and anions may be arranged in the order of the magnitude of their effect on hydration, e.g.,  $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+$ ,  $\text{Cl}^- > \text{NO}_3^-$ . It may thus be seen that this order is the same as that for the effect on viscosity.

The Arrhenius equation :  $\log \eta / \log \eta_0 = \theta C$ , where  $\theta$  is a constant characteristic of the salt and  $C$  is the number of gram-moles of salt per litre, holds with considerable accuracy when tested in view of the hydration theory. The constant  $\theta$  is expressed in terms of apparent molecular hydration  $H$  and a fresh constant  $K$ .

$$\theta = K(H - H_0)$$

$$\text{whence } \log \eta / \log \eta_0 = KC(H - H_0).$$

### 60. The viscosity of aqueous solutions of electrolytes.

M. D. AVASARE and S. M. GAYWALA, Baroda.

Most of the work on the viscosity of aqueous solutions is confined to dilute solutions. Very little being known about the behaviour of concentrated solutions, a knowledge of the behaviour of concentrated solutions is necessary for a complete theory of viscosity.



An attempt is made to compare the viscosities of salt solutions of allied metals, at concentrations ranging from 1M to 4M, and to trace the relation, if any, between viscosity and other properties, such as ionic volumes, hydration, etc. of electrolytes.

It has been observed that electrolytes may be divided into two groups, viz. (1) those which give negative viscosity, and (2) those which always increase the viscosity of water. The aqueous solutions of certain salts of the heavier alkali metals under certain conditions of concentration and temperature produce negative viscosity. The limits of concentration and temperature, within which this phenomena of negative viscosity is observed, depend on the specific nature of the kation and the anion constituting the electrolyte. For the same group of elements increase of atomic weight contributes in a large degree to the observed phenomena of negative viscosity.

The viscosity of electrolytic solutions decreases with a rise of temperature, but does so less rapidly than that of water, so that the relative viscosity increases with a rise of temperature. This observation equally holds for salts which lower the viscosity of water. It is therefore possible that solutions of salts, which at ordinary temperature and concentration increase the viscosity of water, may at suitable concentration and temperature show  $\frac{\eta}{\eta_0}=1$ , and at lower temperature even less than one.

The converse also holds for salts which over a certain range of concentration and temperature lower the viscosity of water.

It has been observed that cations and anions may be arranged in order of the magnitude of their effect on the viscosity of water. For instance  $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+$ ;  $\text{C}_6\text{H}_5\text{COO}^- > \text{CH}_3\text{COO}^- > \text{PO}_4^{3-} > \text{COO}^- > \text{SO}_4^{2-} > \text{C} > \text{NO}_3^-$ .

Of the various changes caused by the rise of temperature, viz. (1) the change in the value of the apparent dissociation of the complex solute molecules, (2) the effect of the increased number of ions in decreasing the complexity of water molecules in addition to the direct effect of the rise of temperature on the latter, (3) thermal decomposition of the hydrate with rise of temperature, and (4) the decrease in the mobility of the ions due to their increased number, the first three of these contribute towards the lowering of the viscosity of the solutions of the electrolytes. Experimental evidence shows that relative viscosity increases appreciably with rise of temperature. This leads one to conclude that the mobility of ions and their specific properties are the predominant factors affecting the viscosity of solutions.

#### 61. The viscosity of mercuric chloride solutions at 35°.

BALBHADRA PRASAD, Cuttack.

The viscosity of mercuric chloride solutions has been measured at 35° by means of Ostwald Viscometer. The concentration ranged from very dilute solutions to almost saturated solutions. In solutions where concentration is greater than 0.4% (0.4 gms. dissolved in 100 c.c. of the solution) the viscosity concentration graph is almost linear. Thus with respect to viscosity also mercuric chloride in solution behaves more like a non-electrolyte than an electrolyte.

#### 62. Studies in salting out effect.

M. D. AVASARE and C. B. PATEL, Baroda.

The salting out of non-electrolytes from aqueous solutions by electrolytes has been generally attributed either to (1) an increase in the internal pressure of the solvent caused by the added electrolyte, or (2) hydration of the electrolyte.



In this part of the investigation, an attempt is made to study and classify the effects of different salts on the salting out of *iso*-amyl alcohol, *iso*-butyl alcohol, aniline and *o*-toluidine in relation to the hydration capacity of these salts.

It has been found that though hydration does not seem to be the only cause for the salting out effect the magnitude of salting out effect generally runs parallel with the hydration capacity of the electrolyte. Further it has been observed that cations and anions stand in the following order with respect to the magnitude of their salting out effect.

$\text{Na}^+ > \text{K}^+ > \text{NH}_4^+$ ;  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ .... and that the same order is observed with respect to their capacity for hydration.

The following equation (Paul M. Gross, chem. rev.; 1933, 13, 92) has been found to hold good over the range 0.25 to 1.0 molar concentration of salt solutions employed in this investigation:—

$$v_a = k_1 C_s,$$

where  $v_a$  is the additional volume in litres of solution which would be required to hold one molecule of a non-electrolyte in solution in presence of the added salt concentrations  $C_s$ , in excess of the volume of water required for its solution in absence of the salt and  $k_1$  is a constant.

Further, it has been observed that the salting out effects of electrolytes in the consecutive members of homologous non-electrolytes bear a constant ratio, given by the expression

$$\frac{s_1}{s_2} = k,$$

where  $s_1$  and  $s_2$  stand for the decrease in the solubility of the non-electrolytes in water caused by the addition of electrolytes.

### 63. The variation of physical properties with changes in the concentration of $\text{HIO}_3$ solution.

M. R. NAYAR, Lucknow.

Experiments on freezing point depression, Raman spectra, etc. indicated polymerization of iodic acid in concentrated aqueous solutions. (*Zeit. anorg. Chemie.*, 1934, 220, pp. 163–171). Confirmatory evidence is available from a systematic study of the various physical properties, such as density, freezing point depression, refractive index, viscosity, and surface tension of solutions varying from 5N to 0.01N. The graphs connecting these properties with concentration are similar, and in no case is the additive law obeyed.

The graph of molecular viscosity ( $\log V^{2/3} \eta - \log \text{conc}^n$ ) is a straight line between 0.01N and 0.5N, after which it rather abruptly changes direction.

Very instructive graphs are obtained for the other properties also.

### 64. The detergent action of soaps.

B. S. KULKARNI and S. K. K. JATKAR, Bangalore.

This paper gives the preliminary results obtained in the course of a comprehensive study of detergents and the detergent action now in progress in our laboratory. We have developed an accurate method of measuring the detergent action of pure soaps by measuring (1) the interfacial tension of benzene and soap solutions with an improved form of inverted pipette for counting the drop number, (2) the viscosities of the emulsions of benzene and water as a measure of adhesion tension,



and (3) by the use of an inactive flocculated colloid like  $\text{Fe}_2\text{O}_3$  instead of carbon black as 'ideal dirt'.

65. The detergency of soap solutions.

B. G. ACHARYA and T. S. WHEELER, Bombay.

In continuation of the work described last year, the maximum efficient adsorption,  $pH$  value, drop number, lathering and wetting powers of dilute soap solutions have been studied. The soaps examined include commercial household soaps, both foreign and Indian; soaps prepared from vegetable oils, and also sodium salts of pure fatty acids. The effect of the addition of various builders on these soaps has also been examined. From the relative adsorption of various soaps on yarn with reference to other properties mentioned, the necessary requirements for a good soap have been deduced. The adsorption value can be used for evaluating the detergency of soap solutions.

66. A lubrication apparatus.

A. NAGARAJA RAO, Bangalore.

The nature of surface films, and the orientation of the molecules in the adsorption layer, have at different times been studied by different investigators employing widely different methods. Hardy has utilized the values obtained for the sliding friction between surfaces to interpret the nature of contact between them, and also the nature and the thickness of the air-cushion separating them under widely different conditions. An apparatus has been constructed by the author for the determination of the sliding friction between different similar and dissimilar surfaces by a measurement of the limiting angle necessary to bring about the sliding of one surface against the other, and when in contact with different substances. The nature of the surface, the material adsorbed, and the extent of adsorption appear to be the chief factors affecting the limiting angle of sliding. The question of the smoothness of different surfaces, however, also makes the values obtained with different surfaces not easily comparable.

It is expected that this apparatus could be made to yield, in the case of lubricants, values which bear a direct relationship to the lubricating property, so that it would be an easy matter to assess the relative efficiencies of different lubricants.

67. A valve potentiometer.

S. K. KULKARNI JATKAR and D. N. MEHTA, Bangalore.

Continuing previous work we have now constructed a three valve amplifier using an electrometer triode as the first stage,  $L_2$  as second, and  $LP_2$  as the last stage, the arrangement being sensitive to a microvolt using a ballistic mirror galvanometer.

68. A thermostat using a gas-filled valve relay.

S. K. KULKARNI JATKAR, Bangalore.

The usual trouble through the sticking of the electromagnetic relays for thermostats can be easily obviated by using the gas-filled relays which can be had for any rating of current. The author has designed a simple arrangement using such a valve.



69. The physical identity of enantiomers. Part III. Viscosities, densities, and refractivities of *d*-, *l*-, and *dl*-forms of isonitrosocamphor (stable and unstable), camphor, camphoric acid, camphoric anhydride, camphorquinone, and sodium camphorate.

B. K. SINGH, KAILASHPATI NARAYAN, PARAMESHWAR SINHA, SHEONATH PRASAD, and NUTBEHARI CHATTERJI, Cuttack.

The viscosities, densities, and refractivities of *d*-, *l*-, and *dl*-forms of camphor and its several derivatives have been examined at 35° at several concentrations. It is found that these properties are identical for the *dextro* and *laevo* isomerides of these compounds: thus Pasteur's Law of Molecular Dissymmetry holds good for these scalar properties also.

The value of these properties for the racemic form of the above-mentioned compounds is different at higher concentrations, but identical at lower: thus indicating the existence of racemates in solution at certain concentrations. In dilute solutions, the racemate is completely dissociated into the optically active components.

The stable (m.p. 153-154°) and the unstable form (m.p. 114-115°) of isonitrosocamphor have been allocated configurations from viscosimetric determinations (cf. Thole, *J. Chem. Soc.*, 1912, 101, 552). The unstable form having the higher viscosity must have the configuration in which the carbonyl and the hydroxyl groups are opposed to each other, whereas the stable form is assigned the configuration in which these groups are adjacent.

## ORGANIC CHEMISTRY.

70. On hydroxy-lactone tautomerism.

CHITTARANJAN BARAT and BASUDEB BANERJEE, Calcutta.

The existence of *ortho*-aldehydic and *ortho*-ketonic acids in the hydroxylactone forms has been proved by the formation of two different series of isomeric methyl esters obtained under different conditions, by various workers among whom the names of Meyer, Kirpal, Wegscheider and Goldschmidt may be mentioned. But so far very meagre attention has been given towards the existence of such forms in open-chain  $\gamma$ - and  $\delta$ -ketonic acids. Experiments with  $\delta$ -ketonic acids like  $\beta$ -phenyl- $\gamma$ -benzoyl- and  $\beta$ -phenyl- $\gamma$ -toluyl-butyric acids have proved the existence of such a pair of tautomeric forms by the formation of two series of methyl esters under different working conditions. The pseudo esters, however, which are in reality the methyl ethers of the lactol forms, are less stable than the normal esters, and are easily convertible into the latter modifications by the action of strong acids and alkalies. The formation of internal anhydrides by the action of acetic anhydride upon these acids also speaks for the existence of these acids in the hydroxylactone forms.

71. Studies in optical isomerism. Part I. Preparation of dextro-*m*-nitrocinnamic acid dibromide.

P. RAMASWAMI AYYAR, Bangalore.

The dextro isomer ( $\alpha_D^{28} = +8.13^\circ$  in methyl alcohol) has been prepared in 30 per cent. yield from inactive (*dl*) *m*-nitrocinnamic acid dibromide by fractional precipitation of the brucine salts.



72. Studies in steric hindrance. Part IX. Oxidative elimination of carboxyl group from 2:4:6-trinitrobenzoic acid with formation of picric acid (2:4:6-trinitrophenol).

J. D. VASAVADA and P. RAMASWAMI AYYAR, Bangalore.

Trinitrobenzoic acid on oxidation with potassium permanganate in acetone solution yields about 15 per cent. of trinitrophenol, identified as such and also by the preparation of acenaphthene picrate. Similar oxidation of 2:4- and 2:6-dinitrobenzoic acids is in progress.

73. Isomerism of acetonedicarboxylic anhydride.

R. P. KANSHAL and S. S. DESHPANDE, Indore.

Pechmann and Neger obtained from acetic anhydride and crude acetonedicarboxylic acid containing a little sulphuric acid dehydracetone-carboxylic acid. Willstatter used pure acetone dicarboxylic acid and obtained its anhydride which melts at  $147^{\circ}$ , which is the melting point of the acid itself. We repeated Willstatter's experiments, but could not get his anhydride. We got, however, another isomeric anhydride melting at  $92^{\circ}$ . This does not behave as a true anhydride. It dissolves in cold alkali from which it is precipitated unchanged by addition of acid. Its hot aqueous solution can, however, be titrated against alkali.

It is probably 2:6-dihydroxy pyrone, for like pyrones, it forms an addition product with mercuric chloride. Moreover, as in pyrones, its carbonyl group is unreactive, while that of the free acid is reactive. Towards aniline, however, it behaves as a true anhydride and gives an acid anilide.

74. The influence of  $\alpha$ -phenyl group in three carbon tautomerism.

N. L. PHALNIKAR and K. S. NARGUND, Ahmedabad.

The object of the present work is to study the effect of  $\alpha$ -phenyl group on the mobility and equilibrium in three carbon tautomerism, and compare it with that of  $\alpha$ -methyl group already noted by Kon and Thakur (*J. Chem. Soc.*, 1930, 2217). The  $\alpha$ -phenyl- $\alpha\beta$ ,  $\beta\gamma$ -unsaturated acids required for this work were prepared by the dehydration of the corresponding  $\beta$ -hydroxy esters obtained by the method of Ivanoff and Nicoloff (*Bull. Soc. Chim.*, 1932, 51, 1325). The study is at present limited to the following compounds:

$\alpha$ -phenyl-cyclopentylidene-(cyclopentenyl) acetic acid,  
 $\alpha$ -phenyl-cyclohexylidene-(cyclohexenyl) acetic acid,  
 $\alpha$  phenyl- $\Delta^{\alpha}(\Delta^{\beta})$ -hexenoic acid.

Experiments on the equilibration of these acids under the standard conditions of Linstead and his co-workers are in progress.

75. Constitutions of phenylglutaconic acids and esters. Part I.  
 $\alpha$ -Phenylglutaconic acid.

N. L. PHALNIKAR and K. S. NARGUND, Ahmedabad.

$\alpha$ -Phenylglutaconic acid has been synthesized by a special method (*Bombay Univ. Jour.*, 1935). It seems to be trans  $\alpha\beta$ -acid as it does not readily yield an anhydride and gives benzoic acid on oxidation by dilute potassium permanganate. Several functional derivatives such as silver, lead, and copper salts, anil, anilic acid, and anhydride have been



prepared. The ethyl ester prepared through the silver salt gives a characteristic sodio derivative when treated with sodium ethoxide or molecular sodium. Experiments on methylation of the sodio derivative are in progress.

76. Condensation of glutaconic acids from phenol and anisole with phenolic ethers.

G. R. GOGTE, Bangalore.

$\beta$ -(4-Methoxy-phenyl)-glutaconic acid adds on easily one molecule of anisole in the presence of dilute sulphuric acid, to produce  $\beta\beta'$ -(4:4'-dimethoxy-diphenyl)-glutaric acid, m.p.  $157^\circ$ ; it is also formed in the condensation of anisole with acetonedicarboxylic acid in the presence of dilute sulphuric acid. Phenol condensed similarly with acetonedicarboxylic acid, giving the  $\beta\beta'$ -(4:4'-dihydroxy-diphenyl)-glutaric acid, m.p.  $235^\circ$  (decomp.); and the dimethoxy derivative of this compound was found identical with the glutaric acid obtained from anisole.

77. Reactivity of formic acid.

L. S. HEBLE and T. S. WHEELER, Bombay.

Previous work on the reactivity of formic acid on compounds containing a reactive halogen atom has been extended. The kinetics of the reaction of anhydrous formic acid with benzyl chloride has been worked out. The formates of sodium, potassium, and ammonium accelerate the reaction. The kinetics of the reaction with acid chlorides is now being studied.

78. Condensation of chloral with acetoacetic ester.

A. A. SHAIKH and the late A. N. MELDRUM, Bombay.

The compound obtained from chloral by condensing it with acetoacetic ester in the presence of pyridine according to Claisen and Mathews (*Annalen.*, 218, 175), gave a product by the action of  $\text{PCl}_5$ , which on reduction by Zn and acetic acid converted the group  $\text{CCl}\cdot\text{CCl}_3$  into  $-\text{CH}\cdot\text{CHCl}_2$ .

79. Condensation of amides with chloral and bromal.

A. M. SHAIKH and the late A. N. MELDRUM, Bombay.

Chloral was directly condensed with cinnamamide, cyanacetamide, and *m*-nitrobenzamide (*cf. Annalen.*, 1871, 157, 245; *Ber.*, 1879, 10, 168) to yield products of the general formula  $\text{RCONH}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$  (I) which gave *acetyl* derivatives with acetic anhydride in sulphuric acid and *anhydrides* with acetic anhydride in NaOH at  $0^\circ$  (*cf. Feist, Ber.*, 1912, 45, 159); *benzoyl* derivatives, *methylethers* were also obtained. The action of  $\text{PCl}_5$  on (I) gave a *monochloro-derivative* which was converted into (I) by water and into a *monoamino-derivative* by ammonia.

Reduction of (I) by zinc and acetic acid converted the group  $-\text{CH}(\text{OH})\cdot\text{CCl}_3$  into  $-\text{CH}=\text{CCl}_2$ .

80. Studies in chloralamides.

N. W. HIRWE and J. S. DESHPANDE, Bombay.

Amides of *o*-, *m*-, and *p*-toluic acids were condensed with chloral and the respective chloralamides  $[\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{OH})\text{CCl}_3]$  obtained. Dimethylsulphate gave methoxy-derivatives, benzoyl chloride gave benzoyl derivatives and anhydro-compounds, acetic anhydride gave



anhydro-compounds and acetyl-derivatives with alkali or concentrated  $\text{H}_2\text{SO}_4$ .

81. The reactivity of  $\alpha$ -chlorine in chloralamides.

N. W. HIRWE and B. V. PATIL, Bombay.

Chloralamide derivatives of 3-bromo, 5-bromo, and 3 : 5-dibromo-salicylic acids and their methyl ethers on treatment with phosphorus pentachloride gave  $\alpha$ -chloro-derivatives  $\text{RCONH}\cdot\text{OHC}\text{Cl}\cdot\text{CCl}_3$  which react with water, methyl alcohol, ethyl alcohol, ammonia, aniline, *o*-, *m*-, and *p*-toluidines.

82. The reactivity of  $\alpha$ -chlorine in chloralamides.

N. W. HIRWE and (MISS) K. D. GAVANKAR, Bombay.

Chloralamide derivatives of 3-nitro-, 5-nitro-, and 3 : 5-dinitrosalicylic acids and their methyl ethers on treatment with phosphorus pentachloride gave  $\alpha$ -chloro-derivatives  $[\text{RCONH}\cdot\text{CH}(\text{Cl})\cdot\text{CCl}_3]$  which react with water, methyl alcohol, ethyl alcohol, ammonia, aniline, *o*-, *m*- and *p*-toluidines.

83. Condensation of bromal with urethanes.

A. A. SHAIKH and the late A. N. MELDRUM, Bombay.

Urethanes have been condensed with bromal in the presence of  $\text{HCl}$  (Bischoff, *Ber.*, 1874, 7, 632). The authors have condensed methyl, propyl, *isobutyl*, and *isoamyl* urethanes with bromalhydrate. The products decompose at higher temperatures; with  $\text{NaOH}$  and acetic anhydride at  $0^\circ$  they yield anhydro-compounds. Action of  $\text{PCl}_5$  on these products gives mono-chloro derivatives which are reconverted into the original compounds by water.

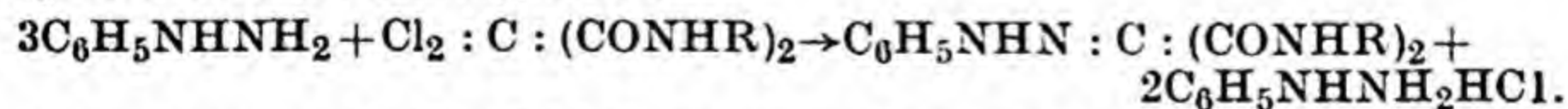
84. Interaction of phenylhydrazine with the halogen derivatives of the substituted amides of malonic acid.

R. K. TRIVEDI and C. M. MEHTA, Baroda.

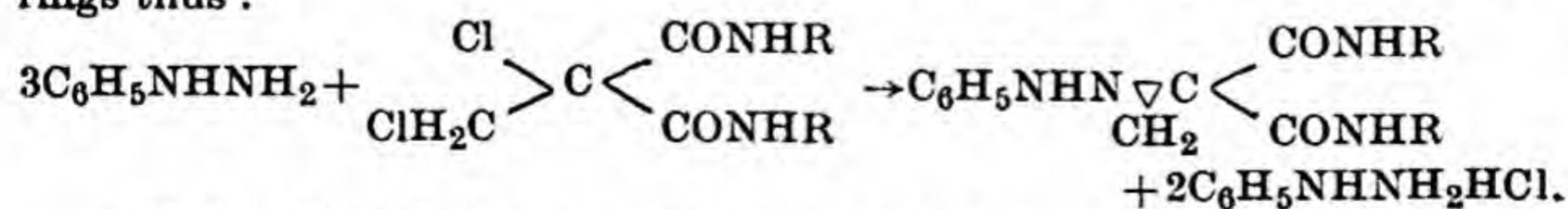
In order to study the labile nature of the chlorine atoms substituting the hydrogens in the reactive methylene group, the interaction of phenylhydrazine with the compounds mentioned below was investigated.

- |  |  |
|--|--|
| (1) Dichloromalon-di-phenylamide                   | (6) Dichloromalon-mono-chloro-phenylamide.             |
| (2) Dichloromalon-di- <i>o</i> -tolylamide.        |  |
| (3) Dichloromalon-di- <i>p</i> -tolylamide.        | (7) Dichloromalon-mono- <i>p</i> -tolylamide.          |
| (4) Dichloromalon-di-1 : 3 : 4-xylidide.           | (8) Chloromethyl chloromalon-di- <i>o</i> -tolylamide. |
| (5) Dichloromalon-di- <i>m</i> -dichlortolylamide. | (9) Chloromethyl chloromalon-di- <i>p</i> -tolylamide. |

The compounds (1), (2), (3) and (4) gave compounds of the type  $\text{C}_6\text{H}_5\text{NHN} : \text{C} : (\text{CONHR})_2$  thus :



Compounds (5) and (6) yielded compounds in which the chlorine in the nucleus remained unaffected, (8) and (9) reacted to give tri-membered rings thus :



All the above hydrazone compounds are very stable.



85. The formation of the sodium derivatives of compounds containing a reactive methylene ( $-\text{CH}_2-$ ) group, and study of the stability of the sodium atom with regard to the methylene carbon atom.

K. G. NAIK and M. L. SHAH, Baroda.

This work was undertaken with a view to studying the formation and the stability of the sodium compounds of the following substituted amides of malonic and methyl malonic acids, and consequently the reactivity of the hydrogens of the methylene group in them :—

- |  |  |
|--|--|
| (1) Malon-di-phenylamide.              | (7) Malon-di- $\beta$ -naphthylamide.      |
| (2) Malon-di- <i>p</i> -tolylamide.    | (8) Malon-di-benzylamide.                  |
| (3) Malon-di- <i>m</i> -tolylamide.    | (9) Malon-di- <i>n</i> -propylamide.       |
| (4) Malon-di- <i>o</i> -tolylamide.    | (10) Methylmalon-di- <i>o</i> -tolylamide. |
| (5) Malon-di-1 : 4 : 5-xylidide.       | (11) Methylmalon-di- <i>p</i> -tolylamide. |
| (6) Malon-di- $\alpha$ -naphthylamide. |  |

They all react with molecular sodium yielding mono-sodium derivatives. In compounds (1) to (9), conversion of the group  $-\text{CH}_2-$  into  $-\text{CHNa}-$  takes place ; whereas in compounds (10) and (11), the conversion of the group  $-\text{CH}(\text{CH}_3)-$  into  $-\text{CNa}(\text{CH}_3)-$  is effected.

Malonamide, malon-mono-phenylamide and malon-mono-*o*-tolylamide remain unreacted.

The above sodium derivatives are comparatively more stable than those of the amides of cyanacetic ester (Naik and Shah, *J. Indian Chem. Soc.*, 1931, 8, 45).

The stability of the sodium atom in the above compounds has been fully studied. When boiled with water, compounds (1) to (8) suffer slow decomposition, the velocity of hydrolysis varying with the groups attached to the nitrogen marked with an asterisk in the following formula :

$\text{H}_2\text{C} : (\text{CONHR})_2$ . The sodium derivatives of (10) and (11) are hydrolyzed more rapidly than the above ones.

86. The velocity of reduction of the chlorines substituting the hydrogens of the reactive methylene group  $-\text{CH}_2-$ , in compounds of the type  $\text{Cl}_2\text{C}(\text{CONHR})_2$ .

R. K. TRIVEDI and C. M. MEHTA, Baroda.

The velocity of reduction of the chlorine atoms was studied by treating the following compounds by means of hydriodic acid generated through the action of HCl on KI (Kurt Meyer, *J. Chem. Soc.*, 1921, 119, 951, 305).

- |  |   |
|--|---|
| (1) Dichloromalon-di-phenylamide.                    | (10) Dichloromalon-monochloro-phenylamide.              |
| (2) Dichloromalon-di- <i>p</i> -tolylamide.          |   |
| (3) Dichloromalon-di- <i>m</i> -tolylamide.          | (11) Dichloromalon-mono- <i>p</i> -tolylamide.          |
| (4) Dichloromalon-di- <i>o</i> -tolylamide.          |   |
| (5) Dichloromalon-di-1 : 3 : 4-xylidide.             | (12) Chloromethyl chloromalon-di-phenylamide.           |
| (6) Dichloromalon-di- $\beta$ -dichlornaphthylamide. | (13) Chloromethyl chloromalon-di- <i>p</i> -tolylamide. |
| (7) Dichloromalon-di-heptylamide.                    | (14) Chloromethyl chloromalon-di- <i>o</i> -tolylamide. |
| (8) Dichloromalon-di-propylamide.                    |   |
| (9) Dichloromalon-di-benzylamide.                    |   |

The velocity of reduction of chlorines is represented by curves, plotting the time of heating along the abscissa and the percentage reduced along the ordinates. It was observed from the nature of the curves of the above compounds that the velocity of reduction goes on increasing from



(1) to (5). This is attributed to the nature of the groups attached to the carbonyl groups between which the  $-CCl_2-$  complex is situated, as well as to the insertion and the position of the methyl groups in the phenyl nucleus. In each case the velocity of reduction is considerably lowered when 50% of the total chlorine is reduced.

The curves of the compounds (7), (8), and (9) indicate that when the radicals attached to the carbonyl group carry an aliphatic chain, the velocity of reduction is increased. If the chain is shorter the velocity of reduction is decreased.

Compounds (10) and (11) show a drop in the velocity of reduction which is due to the presence of only one heavy radical in the complex.

The remarkable decrease in the velocity of reduction of compounds (12), (13), and (14) is attributed to the presence of the  $-ClCH_2-$  grouping.

## 87. Oxidation of alcohols by means of nitrogen peroxide.

P. S. VARMA and C. SATYANARAYAN, Benares.

When methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, and isomyl alcohols are treated with nitrogen peroxide either alone or in presence of substances such as vanadium pentoxide, thorium oxide, cerium oxide and mercuric nitrate, alkyl nitrates are the main products obtained; but when these alcohols are brought in contact with nitrogen peroxide in the gaseous state, specially in presence of vanadium pentoxide, thorium oxide, cerium hydroxide, and mercuric nitrate, varying yields of the corresponding acids are obtained. Vanadium pentoxide gives the best yield of the acids, 85% from ethyl alcohol, 75% from propyl alcohol, 73% from isopropyl alcohol and isobutyl alcohol, 72% from butyl alcohol and 61% from normal primary amyl alcohol.

## 88. Studies on the addition of hydrogen halides to unsaturated conjugated systems.

S. N. GANGULI, Kasauli.

1. Addition of hydrogen bromide to butadiene leads to the production of 1 : 4-bromobutene-2 only.

2. Addition of hydrogen chloride to butadiene leads to the formation of two isomerides, namely (a) 1 : 4-chlorobutene-2 and (b) 1 : 2-chlorobutene-3.

The properties of these addition products have been compared with authentic specimens of the same prepared synthetically, in order to settle their constitution and thereby to locate the position of the new entrants.

An explanation has been advanced to interpret the results obtained in the light of the modern concepts of the electronic theory of valency.

## 89. The action of malonic ester upon isopropylidene malonic ester.

P. C. GUHA and V. K. SUBRAMANIAN, Bangalore.

Molecular proportions of sodio-malonic ester and isopropylidene malonic ester on being heated in a sealed soda water bottle at  $150-60^\circ$  for 24 hours yielded a product, the water soluble portion of which on acidification gave an oil. The aqueous sodium carbonate extract of the oil on acidification and purification by crystallization from alcohol gave a solid, m.p.  $107^\circ$ , of the composition  $C_{11}H_{12}O_6$ . acetyl derivative, m.p.  $82^\circ$ ; it does not give any semicarbazone and seems in all probability to be an interesting dilactone.

From the residual oil after sodium carbonate treatment, isopropylidene dimalonic ester could be smoothly distilled. Action of alkylene



dihalides on the disodium and magnesium derivative of isopropylidene dimalonic ester is under investigation.

90. On cyclization of methylene dimalonic ester.

P. C. GUHA and V. K. SUBRAMANIAN, Bangalore.

Methylene dimalonic ester (1 mol.) on being heated on a water-bath for 4 hours with alcoholic sodium ethoxide (1.2 mol.), and the product being worked up, gave an ester, b.p. 115–18°/3 mm. It gives colouration with ferric chloride and a solid derivative with phenylhydrazine. Work is in progress to elucidate the structure of the compound.

91. Halogenation. Part XIX. The effect of ultraviolet light on the halogenation of some aromatic hydrocarbons.

P. S. VARMA and R. PICHAI, Benares.

Benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and pseudocumene have been brominated in ultraviolet light either alone or in presence of halogen carriers such as aluminium-mercury couple, pyridine, iodine, iron filings, red phosphorus, aluminium chloride, etc., additive as well as substitution products—substitution in the side-chain as well as nucleus—have been obtained in varying yields.

92. Halogenation. Part XVIII. Bromination of toluene.

P. S. VARMA and A. KRISHNAMURTHY, Benares.

Bromination of toluene has been carried on exhaustively in sunlight alone, or in sunlight in the presence of substances such as aluminium dust, aluminium chloride, aluminium-mercury couple, stannic chloride, lanthanum chloride, yttrium chloride, zirconium oxide, thorium chloride, cerium chloride, lead peroxide, red and yellow phosphorus, phosphorus tribromide, vanadium trichloride, yellow sulphur, selenium, tellurium, uranium nitrate, molybdic acid, manganese chloride, potassium permanganate, chromic oxide, iodine, nickel bromide, palladium chloride, iron dust, ferric chloride, and ferric bromide. In accordance with the effect produced on bromination, the above substances can be divided into four classes :

- (i) those that have no effect on bromination at all, i.e. the products obtained being the same as those obtained in sunlight alone ;
- (ii) those that yield only *p*-substituted nuclear compounds with a certain quantity of the side-chain substituted halogen derivatives ;
- (iii) those that yield both *o*- and *p*-substituted nuclear compounds only, the *p*-substituted derivative predominating in some cases and the *o*-substituted in others ;
- (iv) those that yield both *o*- and *p*-substituted nuclear derivatives as well as side-chain substituted ones.

93. Bromination of substances containing two aromatic nuclei. Part III. Bromination of substituted phenyl salicylates.

Y. I. RANGWALA and G. V. JADHAV, Bombay.

In continuation of previous work (*Proc. Ind. Acad. Sciences*, 1935, I, 616, and *J. Indian Chem. Soc.*, 1935, 12, 89) *p*-cresyl salicylate, *p*-nitro-phenyl salicylate, and *p*-chloro-phenyl salicylate were prepared and brominated. The brominated compounds were purified and found identical with *p*-cresyl-5-bromo-salicylate (m.p. 96–99°), *p*-cresyl 3 : 5-



dibromo-salicylate (m.p.  $151^{\circ}$ ), *p*-nitro-phenyl-5-bromo salicylate (m.p.  $213^{\circ}$ ) and *p*-chloro-phenyl-5-bromo salicylate (m.p.  $102-104^{\circ}$ ). The above esters were prepared for identification from 3-bromo- and 3 : 5-dibromo salicylic acid and the different cresols and phenols. The above results show the strong directing influence of the OH group in the salicylic acid nucleus over that of  $\text{CH}_3$  and Cl group apart from the deactivation caused by the presence of the nitro group in *p*-nitrophenylsalicylate.

94. o-Aldehydo-carboxylic acids. Part III. A synthesis of 4 : 5-methylene-dioxypthalaldehydic acid.

S. N. CHAKRAVARTI and M. SWAMINATHAN, Annamalainagar.

4 : 5-Methylenedioxyphthalaldehydic acid, for the synthesis of which an unsuccessful attempt was made in 1927 by Stevens and Robertson (*J. Chem. Soc.*, 1927, 2791), has now been synthesized from 4 : 5-methylenedioxyhomophthalic acid, which in its turn was prepared from piperonal through the corresponding hydrindone. 4 : 5-Methylenedioxyhomophthalic acid on oxidation with selenium dioxide in benzene solution gave the corresponding phthalonic acid, the aniline derivative of which on being boiled with dry xylene was transformed into anilo-4 : 5-methylenedioxyphthalaldehydic acid, m.p.  $187^{\circ}$ . The latter on hydrolysis gave 4 : 5-methylenedioxyphthalaldehydic acid, m.p.  $167^{\circ}$ . The aldehydo-acid on reduction with sodium amalgam gave 4 : 5-methylenedioxyphthalide, m.p.  $189^{\circ}$ , which was also obtained by decarboxylating 4 : 5-methylenedioxyphthalidecarboxylic acid, m.p.  $223^{\circ}$ , obtained by the reduction of 4 : 5-methylenedioxyphthalonic acid.

95. On some polybasic acids.

P. K. PAUL, Calcutta.

The following experiments were performed in order to prepare some intermediate products which were required in a scheme of synthesis of Cochinellie acid.

*m*-Cresol was condensed with chloroform in presence of caustic soda solution giving rise to 2-hydroxy 4-methyl benzaldehyde (b.p.  $219^{\circ}-221^{\circ}$ ) which was methylated with methyl iodide. The 2-methoxy 4-methyl benzaldehyde (b.p.  $250^{\circ}-253^{\circ}$ ) thus obtained was condensed with malonic acid to yield the corresponding cinnamic acid derivative (m.p.  $211^{\circ}-212^{\circ}$ ). This was then reduced to the hydrocinnamic acid derivative (m.p.  $95^{\circ}$ ).

The constitution of 2-methoxy-4-methyl-benzaldehyde has been verified by its synthesis from methoxy-*m*-cresotinic acid, which was in turn converted into the amide (m.p.  $143^{\circ}$ )—nitrile (m.p.  $71^{\circ}$ )—aldehyde (b.p.  $251^{\circ}-252^{\circ}$ ) and cinnamic acid (m.p.  $211^{\circ}-212^{\circ}$ ).

96. The synthesis of coumarins and chromones from phenols and  $\beta$ -ketonic esters : Coumarins and chromones from 4-chloro-1-naphthol.

D. CHAKRAVARTI and P. BAGCHI, Calcutta.

In view of the work of Dey and Lakshminarayana (*J. Indian Chem. Soc.*, 1932, 9, 153), who obtained a chromone by condensing  $\beta$ -naphthol with acetoacetic ester using  $\text{H}_2\text{SO}_4$  as condensing agent, and the observations of one of us (Chakravarti, *J. Indian Chem. Soc.*, 1932, 9, 32) that chloro-, bromo-, and nitro-phenols yield chromones according to Simonis' method using phosphorus pentoxide, the condensations of the halogenated and nitronaphthols ( $\alpha$ - and  $\beta$ -) with  $\beta$ -ketonic esters have been studied.

4-Chloro-1-naphthol (Kast, *Ber.*, 1911, 44, 1337) has been condensed with acetoacetic ester and its C-alkyl derivatives using sulphuric acid



(Pechmann's reaction) or phosphorus pentoxide (Simonis' reaction). In the presence of sulphuric acid coumarins are always formed, but the yield diminishes markedly with a heavier substituent in the acetoacetic ester molecule. When phosphorus pentoxide is used 4-chloro-1-naphthol gives coumarins with unsubstituted acetoacetic ester, but C-methyl-, C-ethyl-, and other C-alkyl-acetoacetic esters give a good yield of chromones forming characteristic styryl derivatives.

97. Preparation of higher fatty-acyl derivatives of  $\alpha$ -naphthylamine.

P. S. VARMA and C. SRINIVASMURTHYACHAR, Benares.

Attempts have been made with success for the preparation under ordinary conditions of caproic, caprylic, lauric, myristic, palmitic, and stearic acid derivatives of  $\alpha$ -naphthylamine which have been obtained before by heating at high temperatures in sealed tubes.

98. Studies in the chemistry of amidines.

A. P. KHANOLKAR and T. S. WHEELER, Bombay.

By condensing benzotrichloride with *m*-toluidine in nitrobenzene, *di*-(*m*-tolyl)-benzamidine was obtained. With chloroformic ester it gave a product of the formula  $C_6H_5C(:NC_6H_4CH_3)(\cdot NC_6H_4CH_3)(COOEt)$ . Di-(*m*-tolyl)-benzamidine, di-(*p*-nitro-phenyl)-benzamidine and di-(*m*-nitro-phenyl)-benzamidine were methylated and methyl derivatives obtained.

On oxidation, diphenyl-benzamidine gave a compound of the constitution  $[C_6H_5C(:NC_6H_5)(\cdot NC_6H_5)]_2$ .

*N'*-(*p*-nitro-phenyl)-*N*-(*p*-methoxy-phenyl)-benzamidine, *N'*-(*di*-*m*-*p*-methyl-phenyl)-*N*-(*p*-nitrophenyl)-benzamidine, *N'*-(*m*-nitrophenyl)-*N*-(*p*-nitro-phenyl)-benzamidine have been prepared. The tautomerism of the amidines is being studied.

99. Studies in the chemistry of amidines.

S. P. JOSHI and T. S. WHEELER, Bombay.

(1) Di-(*p*-chloro-phenyl)-benzamidine, (2) *N'*-(*p*-chloro-phenyl)-*N*-(phenyl)-benzamidine, (3) *N'*-(*p*-ethoxy-phenyl)-*N*-(*p*-chloro-phenyl)-benzamidine, have been prepared and methylated. Indication of the formation of two methyl derivatives has been obtained with (2) and (3). The tautomerism of other unsymmetrical amidines is being investigated.

100. Styryl-amidines.

R. C. SHAH and M. M. SIDIKI, Bombay.

As styryl-amidines have not hitherto been prepared, a number of typical styryl-amidines, which were also required in connection with other work, have been prepared for an examination of their chemical properties by condensation of cinnamanilides with arylamines in the presence of phosphorus trichloride. The following amidines have been obtained: Diphenylcinnamamidine, phenyl-*p*-tolyl-cinnamamidine, phenyl-*o*-tolyl-cinnamamidine, phenyl-*m*-tolyl-cinnamamidine, phenyl-*p*-methoxy-phenyl-cinnamamidine, phenyl-*p*-ethoxy-phenyl-cinnamamidine, Di-(*p*-methoxyphenyl) cinnamamidine, di-(*p*-ethoxy phenyl) cinnamamidine. All the amidines are yellow crystalline solids. Some reactions of the amidines including bromination and reduction have been studied.



101. Imido-chlorides. Condensation of *N*-phenylurethane with benzanilideimidochloride.

R. C. SHAH and H. P. GHADIALI, Bombay.

Benzanilideimido-chloride, when condensed with the sodium derivative of *N*-phenylurethane in ethereal medium, gave the condensation product phenyliminobenzyl-*N*-phenyl urethane, m.p. 86°, whose constitution was proved by its synthesis from diphenylbenzamidine and ethyl chloroformate. Various reactions of the condensation product have been studied. The action of bromine gave a dibromo addition product, and the action of aromatic amines gave characteristic derivatives. It is easily hydrolyzed by hydrochloric acid into benzanilide and phenylurethane. Reduction by aluminium amalgam yielded the reduction product, which is readily and smoothly hydrolyzed to give benzaldehyde in almost theoretical yield. This provides a valuable new method for the conversion of an aromatic carboxylic acid into the corresponding aldehyde.

## 102. Imido-chlorides. Reactions of oxanilideimidochloride.

V. R. HEERAMANECK and R. C. SHAH, Bombay.

Oxanilide-imido-chloride was prepared according to the method of Bauer (*Ber.*, 1907, 40, 2653). With aniline it afforded the corresponding diamidine, m.p. 156–158° (hydrochloride m.p. 242°). On condensation with ethylsodiummalonate in toluene, it gave the condensation product, m.p. 128–130°, which has been cyclized by the action of heat into 4:4'-dihydroxy-3:3'-dicarbethoxy-2:2'-diquinonyl, m.p. above 300°. Condensation with the sodium derivative of urethane, yielded a crystalline product, which is being investigated.

## 103. Condensation of epichlorhydrin with resacetophenone.

D. R. NADKARNI and T. S. WHEELER, Bombay.

In continuation of the work with glyceryl chlorhydrin described last year, the above condensation was investigated and found to give three *ethers* under suitable conditions: chlorhydrin ether, mono-glycide ether, di-glycide ether. The former two gave on hydrolysis the mono-ether obtained in the condensation of glyceryl chlorhydrin with resacetophenone. These ethers can be converted into one another under suitable conditions.

The *chalkones* obtained from the mono- and di-ethers from the latter condensation, gave on treatment with selenium dioxide *mono-* and *di-flavones*, while with hydrogen peroxide they gave *mono-* and *di-flavonols*.

104. Reactivity of *p*-anisylidene-*p*-methylacetophenone.

S. M. NADKARNI and T. S. WHEELER, Bombay.

The dibromide (II) of 4-methoxystyryl-*p*-tolylketone (I) gives when heated with methyl and ethyl alcohols  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -4-methoxyphenyl- $\beta$ -methoxyethane (III) and  $\alpha$ -toluoyl- $\alpha$ -bromo- $\beta$ -4-methoxyphenyl- $\beta$ -ethoxyethane (IV) respectively. With excess of bromine, (I) yields the dibromide of 4-methoxy-3-bromo-styryl-*p*-tolylketone (V), which with methyl and ethyl alcohols gives respectively  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -4-methoxy-3-bromo-phenyl- $\beta$ -methoxyethane (VI) and  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -4-methoxy-3-bromo-phenyl- $\beta$ -ethoxyethane (VII). (V) with potassium iodide in acetone gives 4-methoxy-3-bromo-styryl-*p*-tolylketone (VIII) the constitution of which will be confirmed by its synthesis from 3-bromo-*p*-anisaldehyde and *p*-methylacetophenone. (II) with pyridine gives  $\alpha$ -toluoyl- $\alpha$ -bromo- $\beta$ -4-methoxyphenylethylene (IX) and it is also obtained by heating (III) or (IV). (V) with pyridine



gives  $\alpha$ -toluoyl- $\beta$ -4-methoxy-3-bromophenylethylene (X) which is also obtained by heating (VI) or (VII). (II) and (V) with KCN in alcohol yield  $\beta$ -*p*-toluoyl- $\alpha$ -4-methoxyphenylpropionitrile (XI) and  $\beta$ -*p*-toluoyl- $\alpha$ -4-methoxy-3-bromophenylpropionitrile (XII) respectively. (XI) is also obtained from (I) and HCN.

### 105. Reactivity of piperonylidene-*p*-methyl-acetophenone.

A. M. WARRIER and T. S. WHEELER, Bombay.

The dibromide (I) of 3 : 4-methylenedioxy-styryl-*p*-tolyl-ketone (II) when boiled with methyl and ethyl alcohols gives respectively,  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -3 : 4-methylenedioxyphenyl- $\beta$ -methoxy-ethane (III) and  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -3 : 4-methylenedioxyphenyl- $\beta$ -ethoxy-ethane (IV). With excess of bromine, (II) yields the dibromide of 3 : 4-methylenedioxy-6-bromo-styryl-*p*-tolyl ketone (V). This with methyl and ethyl alcohols gives respectively,  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -3 : 4-methylenedioxy-6-bromo-phenyl- $\beta$ -methoxy-ethane (VI) and  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -3 : 4-methylenedioxy-6-bromo-phenyl- $\beta$ -ethoxy-ethane (VII). (V) with potassium iodide in acetone gives 3 : 4-methylenedioxy-6-bromo-styryl-*p*-tolyl ketone (VIII), the constitution of which is fixed by its synthesis from 6-bromo-piperonal and *p*-methyl-acetophenone. (I) and (V) with pyridine give respectively,  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -3 : 4-methylenedioxyphenyl-ethylene (IX) and  $\alpha$ -*p*-toluoyl- $\alpha$ -bromo- $\beta$ -3 : 4-methylenedioxy-6-bromo-phenyl-ethylene (X). (X) is also obtained from (V) by the action of one molecule of sodium methylate. (I) and (V) with KCN in alcohol yield respectively,  $\alpha$ -3 : 4-methylenedioxyphenyl- $\beta$ -*p*-toluoyl-propionitrile (XI) and  $\alpha$ -3 : 4-methylenedioxy-6-bromo-phenyl- $\beta$ -*p*-toluoyl-propionitrile (XII). (XI) has been synthesized from (II) and HCN.

### 106. Condensation of phenols with succinic anhydride.

J. D. RAVAL and K. S. NARGUND, Ahmedabad.

Various phenols have been condensed with succinic anhydride by Friedel and Craft's method using acetylene tetrachloride as the solvent.

Phenol gave  $\gamma$ -keto- $\gamma$  : 2-hydroxy-phenyl-butyric acid, m.p. 146° identical with the acid described by Rosenmund and Schapiro (Arch. Pharm., 1934, 313).

*o*-Cresol gave two products: (i)  $\gamma$ -keto- $\gamma$  : 2-hydroxy-3-methyl-phenyl-butyric acid, m.p. 136°, (ii)  $\gamma$ -keto- $\gamma$  : 4-hydroxy-5-methyl-phenyl-butyric acid, m.p. 184°.

*m*-Cresol gave  $\gamma$ -keto- $\gamma$  : 2-hydroxy-4-methyl-phenyl-butyric acid, m.p. 154°.

*p*-Cresol gave  $\gamma$ -keto- $\gamma$  : 2-hydroxy-5-methyl-phenyl-butyric acid, m.p. 137°, identical with the acid described by Rosenmund and Schapiro (*loc. cit.*).

The constitutions of the above keto acids were determined by first converting the phenolic group into the methoxy group and then oxidizing the methoxy compound. All the acids were characterized by the preparation of derivatives, such as methyl ester, ethyl ester, phenylhydrazones, etc. Further work on the condensation of substituted phenols and naphthols is in progress.

### 107. Condensation of nitro-phthalic anhydrides with phenol and anisole.

P. C. MITTER and P. C. DATTA, Calcutta.

3-Nitrophthalic anhydride condenses with phenol, in presence of aluminium chloride, giving 3-nitro-2 (2'-hydroxybenzoyl)-benzoic acid. On reduction, followed by diazotization and ring closure, it gave chrysazin.



Curiously enough, 4-nitrophthalic anhydride could not be condensed with phenol under the same conditions.

3-Nitrophthalic anhydride condensed readily with anisole, giving two products, among which 3-nitro-2 (4'-methoxybenzoyl)-benzoic acid predominates. With 4-nitrophthalic anhydride and anisole a mixture of 4-nitro-2 (4'-methoxybenzoyl)-benzoic acid and 5-nitro-2 (4'-methoxybenzoyl)-benzoic acid is obtained.

#### 108. Studies in the isoflavone series.

P. C. MITTER and S. S. MAITRA, Calcutta.

$\beta$ -Resorcyraldehyde dimethyl ether condenses with hippuric acid in presence of sodium acetate and acetic anhydride giving an azlactone, m.p. 168°, which on hydrolysis gave 2:4-dimethoxyphenyl pyruvic acid, m.p. 156°. This was converted over its oxime, m.p. 145°, into 2:4-dimethoxy phenylacetone, m.p. 76°. This was condensed with phloroglucinol, giving 2':4'-dimethoxyphenyl-2:4:6-trihydroxyacetophenone, m.p. 175°. Attempts at conversion into isoflavone by treatment with ethyl formate and molecular sodium failed. On heating with sodium acetate and acetic anhydride, followed by hydrolysis, we obtained 2-methyl-5:7-dihydroxy-2':4'-dimethoxy-isoflavone, m.p. 213-214°.

#### 109. Condensation of bromo-salicylaldehydes with phenols and amines.

K. S. VENKAT RAMAN and P. S. VARMA, Benares.

The condensation of aldehydes with phenols has been previously studied by several investigators. By condensing 1 molecule of the aldehyde with 2 molecules of the phenols in presence of sulphuric acid (d. 1.840) at about 100°, Sen and Sinha (*J. Amer. Chem. Soc.*, 1923, 2984) obtained the corresponding fluorones at one stage. In the present paper 5-bromo-, 3:5-dibromo-, and 3-bromo-5-nitro-salicylaldehydes have been condensed with various phenols like resorcinol, pyrogallol, etc. and phenolic acids like gallic acid according to the above method. The condensation products are generally fluorescent and possess dyeing properties. These products on bromination yield compounds which are much deeper in colour.

The above aldehydes have been condensed with 2 molecules of dimethyl- and diethyl-anilines in presence of fused zinc chloride or concentrated hydrochloric acid to yield triphenyl methane dyes. The leuco bases are green in colour and these on oxidation give green dyes.

#### 110. The condensation of aldehydes with malonic acid in the presence of organic bases. Part IV. The condensation of piperonal and the formation of piperonal-acrylic acid.

K. C. PANDYA and T. A. VAHIDY, Agra.

In the studies of the condensation of piperonal with malonic acid in the presence of traces of pyridine, the yield of the unsaturated acid was found to be theoretical (Kurien and Pandya, *J. Indian Chem. Soc.*, 1934, 11, 825). The condensation has now been investigated in the presence of a large number of organic bases and also of ammonia and ammonium malonate (Knoevenagel). The organic bases tried were: aniline; *o*-, *m*- and *p*-toluidine;  $\alpha$ - and  $\beta$ -naphthylamine; piperidine, methylaniline, ethylaniline, diphenylamine; pyridine, lutidine, quinoline, isoquinoline, quinaldine, diethylaniline, and dimethylaniline. In every case the base was 0.15 molecular proportion, this being increased to 0.25 mole also in the case of piperidine. Good yields, up to 97%, were



obtained. The piperonylacrylic acid, even after repeated purifications, melted at  $242^{\circ}$  (decomp.), and its identity was confirmed by analysis. The m.p.s recorded by earlier workers were lower (cf.  $232^{\circ}$ , Lorenz, *Ber*, 13, 757;  $238^{\circ}$ , Perkin, *J. Chem. Soc.*, 1891, 152;  $232^{\circ}$ , Dutt, *J. Indian Chem. Soc.*, 1925, 1, 300;  $240^{\circ}$ , Kurien, *loc. cit.*).

111. Interaction of sulphuryl chloride with compounds containing two aromatic nuclei.

D. R. SUKHATANKAR and G. V. JADHAV, Bombay.

The work described last year (*Ind. Science Congress, Chem. Abst.*, 1935, 31) has been extended to the benzoyl derivatives of *p*-phenetidine, *p*-anisidine, *m*-xylidine, and naphthylamines.

Sulphuryl chloride acts as the chlorinating agent in each case and chlorine enters the basic nucleus. The nitro benzoyl derivatives of *o*, *m*, and *p*-toluidines have also been investigated with similar results.

112. Derivatives of hydroxy-naphthoic acid.

S. N. RAO and G. V. JADHAV, Bombay.

Extending the work previously communicated, chlorination and bromination of 1-methoxy-2-naphthoic acid was carried out. The constitutions of the resulting products have been established and a number of derivatives prepared.

Bromination of the arylamides of 1-hydroxy-2-naphthoic acid was carried out in stages when mono- and dibromo compounds were obtained. The constitutions of these compounds have been confirmed by synthesis.

113. Action of hydrogen sulphide on chalcone oxides.

MISS B. N. KATRAK and T. S. WHEELER, Bombay.

When chalcone oxides are heated with  $H_2S$ , the oxide ring is opened and hydroxy-mercaptan derivatives are formed. An examination of the products obtained in this way from a number of chalcones is in progress.

114. Chalkones and flavones from 2-acetyl-resorcinol.

I. Z. SAIYED and T. S. WHEELER, Bombay.

2-Acetyl-resorcinol has been condensed with benzaldehyde, salicylaldehyde and *o*-chloro-benzaldehyde in presence of alkali. The condensation products are mixtures of chalkones and flavanones. The condensation of acetyl- $\beta$ -methyl-umbelliferone with various aldehydes is also being examined.

115. Additive compounds of chlor-acetic acids with a few amines.

K. S. VENKAT RAMAN, Benares.

When warm benzene solutions of *o*-chloro-aniline, *p*-chloro-aniline, and  $\beta$ -naphthylamine are treated with mono-, di-, and trichloroacetic acids in the same solvent and allowed to cool, needle-shaped crystalline additive compounds are obtained. The readiness with which the pure additive products could be prepared and their sharp m.p.'s make them useful for the identification of these amines. All the compounds are white turning grey on exposure for a long time, difficultly soluble in the ordinary solvents, easily soluble in alcohol and water. Strong alkalis generate the respective bases.



## 116. The action of caustic alkali on 7-hydroxy-coumarin-4-acetic acid.

N. V. BHIDE, Poona.

While trying to prepare  $\beta$ -(2:4-dihydroxy-phenyl)-glutaconic acid by the application of Limaye and Bhawe's method (*J. Indian Chem. Soc.*, 1931, 8, 139) to resorcin, it was observed that 7-hydroxy-coumarin-4-acetic acid titrated apparently as a dibasic acid owing either to the OH group taking part in the titration or the opening of the pyrone ring. To decide this point the silver salt of the acid was prepared. This after treatment with methyl iodide gave the methyl ester of 7-methoxy-coumarin-4-acetic acid, m.p.  $121^{\circ}$ - $122^{\circ}$ , which on hydrolysis gave the known 7-methoxy-coumarin-4-acetic acid, m.p.  $187^{\circ}$ - $190^{\circ}$ , which titrated as a monobasic acid and, on decarboxylation, gave the methyl ether of 4-methyl-umbelliferone, m.p.  $160^{\circ}$  showing that the OH group took part in the titration.

Next the acid was boiled with 2*N*-caustic soda before preparing the silver salt. Still the same results were obtained on methylation, etc.; indicating that the structure assigned to the silver salt by Dey (*J. Chem. Soc.*, 1915, 1632) as the disilver salt of  $\beta$ -(2:4-*m*-dihydroxy phenyl)-glutaconic acid does not seem to represent the fact. It should instead be represented as the disilver salt of 7-hydroxy-coumarin-4-acetic acid. The work is being continued.

## 117. The reactivity of conjugated systems. Part VII. Condensation of 1:2-diketones with cyanoacetamide.

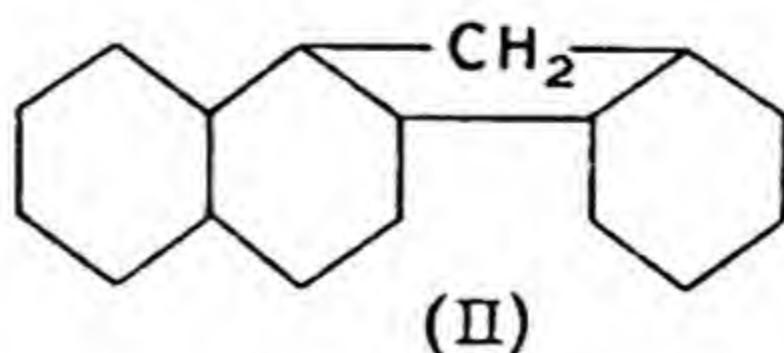
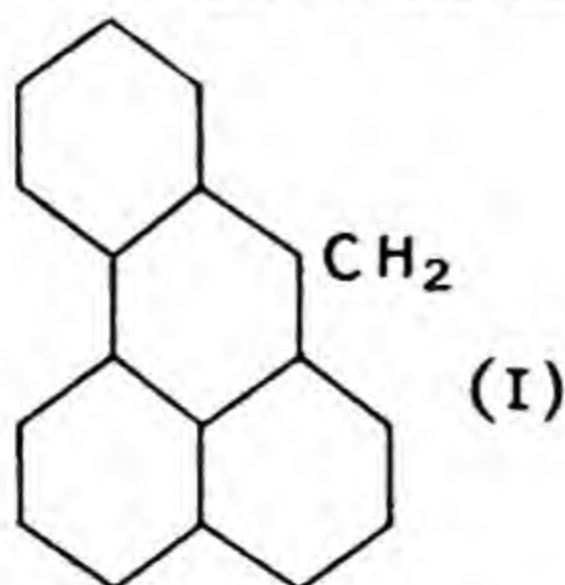
CHITTARANJAN BARAT and BASUDEB BANERJEE, Calcutta.

This type of reaction has not been undertaken so far, except in the case of benzil (MacRae and Kuchnern, *J. Amer. Chem. Soc.*, 1930, 52, 3379), where the absence of a labile hydrogen atom precludes the formation of an enolic phase, and consequently it reacts purely in the ketonic form in the usual way.

In the course of the present work the condensation has been carried out with such 1:2-diketones that possess an enolic phase, e.g. *o*-cyclo-hexane- and *o*-cyclo-pentane-dione, diacetyl, etc. The reaction proceeds in the manner described in earlier works of this series, the ethylenic linkage getting preference over the ketonic, such that the primary addition takes place at the ethylenic bond followed by the elimination of water between the enolic hydroxyl and the amino groups. That one of the ketonic groups is left intact is proved by the formation of semicarbazones from the condensation products. The work has also been extended towards *ortho*-quinones, e.g. phenanthraquinone, acenaphthaquinone, etc. Here, however, the condensation takes place through the ketonic groups only for reasons stated above.

## 118. On a new synthesis of isochrysofluren and chrysofluren.

NRIPENDRANATH CHATTERJI, Calcutta.



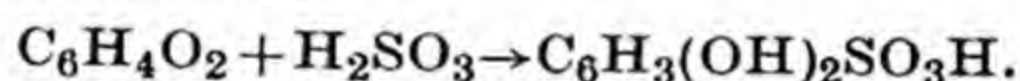


Ethyl 1- $\alpha$ -naphthyl-2-methyl-2-carboxy-*cyclohexanol* (b.p. 220°-25°/6 mm.) was obtained by the action of  $\alpha$ -naphthylmagnesium bromide on ethyl 2-methyl-2-carboxy-*cyclohexanone*. This on dehydration by Dargen's method yielded ethyl 1- $\alpha$ -naphthyl-2-methyl-2-carboxy-*cyclohexene* (b.p. 210°-220°/6 mm.). The acid (b.p. 235°-245°/7 mm.) obtained on hydrolysis was subjected to the action of zinc chloride (anhydrous) when methyl-trihydro-peri-benzanthrone was obtained (b.p. 215°-225°/4 mm.). It is expected that the product obtained by the reduction of peri-benzanthrone derivative by means of P and HI will give the required *isochrysofluoren* (I) on heating with selenium. Similarly it is expected that from  $\beta$ -naphthylbromide and ethyl 2-methyl-2-carboxy-*cyclohexanone* *chrysofluoren* (II) will be obtained.

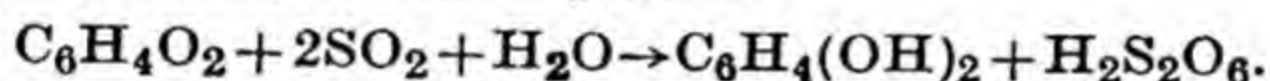
### 119. Formation of quinol sulphonic acid and dithionic acid during hydroquinone development.

K. M. PANDALAI, Bangalore.

Opinion has been divided regarding the formation of quinolsulphonic acid and dithionic acid in developing solutions. The results of Pinnow (1913), Bogisch and Andreson (1900), and Dodgson (1914) have now been confirmed by the actual isolation of quinolsulphonic acid as its sodium salt ( $C_6H_5O_5SNa$ ) from developing solutions on use as white leaflets crystallizing from methyl alcohol. The substitution of  $SO_3H$  groups in the benzene nucleus in this case is probably an instance of 'indirect addition' (cf. Wöhler, 1844):



But Mees and Sheppard (1902) are inclined to the view that dithionic acid is formed according to the equation:



Several workers have failed to obtain dithionic acid, which must evidently be due to (i) the extreme instability of dithionic acid, and (ii) the quantity formed being very minute. The writer was able, however, to obtain this acid as the barium salt, but only on one occasion. Nabl (1901) considers the formation of dithionic acid as probable.

### 120. Studies in bridge formation.

P. C. GUHA, Bangalore.

The bridging of succinosuccinic ester with methylene iodide and ethylene bromide was first tried by Baeyer (*Ber.*, 1892, 25, 2123), evidently without success.

Dry sodio-derivative of succinosuccinic ester when boiled under reflux during 72 hours with ethylene and trimethylene bromide yields the expected bridged compounds, m.p. 112° and 132°. That the reactions have not taken place in the enolic phase is proved by the fact that the bridged compounds give disemicarbazones. The bridged esters can be converted into the corresponding diacids by boiling with 50% HCl. It is interesting to note that the bridged diesters and the diacids cannot be easily decarboxylated, and this behaviour is in marked contrast to that of succinosuccinic ester which gives 1:4-diketohexamethylene on being heated with water at 200°.

The compound obtained by the action of iodine or bromine on succinosuccinic ester and to which a bridged structure was given before (Gaird and Guha, *Sci. Cong. Abstracts*, 1934) has been proved to be dihydroxy terphthalic ester. This observation is important because it proves the instability of Dewar's structure of benzene which immediately on formation



by the present method rearranges into the ordinary Kekule phase (cf. Ingold, *J. Chem. Soc.*, 1922, 121, 1135).

Tetramethyl- and dimethyl-succinosuccinic esters are being prepared by the action of sodium on asym-dimethyl- and monomethyl-succinic esters which are expected to yield interesting bridged compounds.

### 121. Synthetic experiments in the pinene group. Part I. Synthesis of *cis*pinononic acid and ketonopinone (4:6-diketopinane).

P. C. GUHA and K. GANAPATHI, Bangalore.

A series of synthetic experiments starting from norpinic acid have been instituted with the object of synthesizing pinene and its important degradation products. *Trans*-norpinic acid, obtained by the method of Kerr with slight modifications, is converted by means of acetic anhydride into *cis*-norpinic anhydride which with an equimolecular quantity of sodium methoxide gives the sodium derivative of *cis*-norpinic acid monomethylester. The acid chloride of this acid ester, prepared by treatment with thionyl chloride, furnished with zinc methyl iodide *cis*-methylpinononate and a small amount of a solid, m.p. 72–74°. The ester on hydrolysis yields *cis*-pinononic acid.

Methyl pinononate on treatment with sodium in toluene solution or sodium ethoxide in alcoholic solution smoothly undergoes cyclization yielding 'ketonopinone' (4:6-diketopinane) which exhibits all the properties of a  $\beta$ -diketone and gives a copper derivative. The constitution of this compound is confirmed by hydrolyzing it to pinononic acid with baryta. Work is in progress for the reduction of this diketone to nopinone and nopinane. This is the first total synthesis of a bicyclic compound of the pinene series.

### 122. Synthetic experiments in the pinene group. Part II.

P. C. GUHA and K. GANAPATHI, Bangalore.

As an alternative route to ketonopinone, *cis*-norpinic acid diethyl ester is condensed with ethyl acetate in presence of sodium whereby an oil, b.p. 66–67°/6 mm., and an undistillable product are obtained, the former exhibiting properties of a  $\beta$ -ketonic ester.

The synthesis of *cis*-4:4-dimethyl-1:3-diacetylcyclobutane, which on dehydration is expected to yield verbenone, has not so far been achieved from *cis*-norpinic diacid chloride by the action of either MgMeI or ZnMeI. In the former case, an undistillable neutral product with a strong terpene like odour and in the latter a neutral (probably a lactonic) product crystallizing in needles, m.p. 96°, together with an oil were obtained, none of which gave semicarbazones.

Another synthesis of nopinone through the following steps is in progress: *cis*norpinic anhydride  $\rightarrow$  ethyl norpinylmalonate  $\rightarrow$  pinylmalonic acid  $\rightarrow$  *unsym.* homopinonic acid  $\rightarrow$  nopinone.

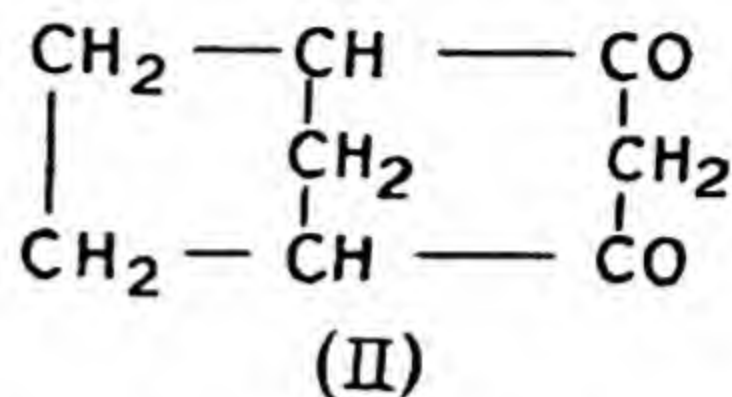
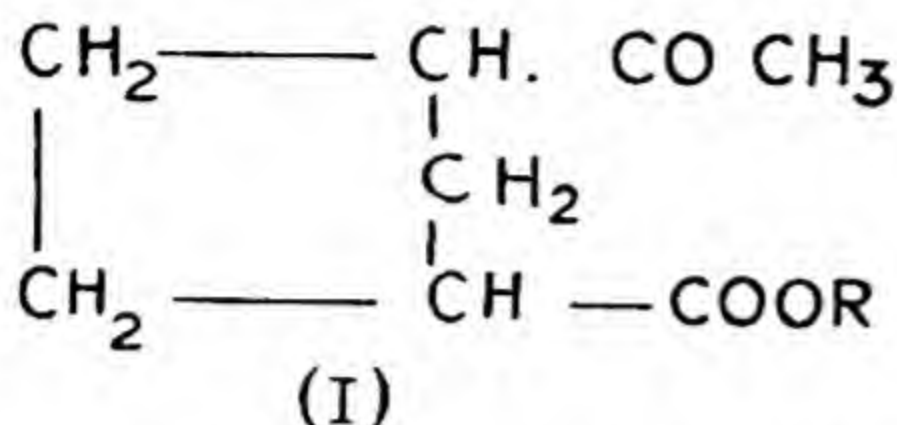
### 123. Bicyclo-(1:2:3)-octane-2:4-dione.

P. C. GUHA and S. K. RANGANATHAN, Bangalore.

Semmler and Bartelt's (*Ber.*, 1907, 40, 4596) 1-acetylcyclopentane-3-carboxylic acid (I, R=H) obtained by oxidizing santene has been synthesized starting from *cis*-cyclopentane-1:3-dicarboxylic anhydride. The great difficulty attending the preparation of the starting material by the older methods has been overcome by subjecting the cyclic tetra-ester to



the action of 50% hydrochloric acid resulting in the formation, in one stage, of *cis* and *trans* diacids.



The monoacid monomethyl ester obtained from the *cis* anhydride by the action of methyl alcohol gives the corresponding acid chloride (*p*-toluidide, m.p. 118.5°) which furnishes the ketonic ester (b.p. 99-100°; I, R=CH<sub>3</sub>; semicarbazone, m.p. 138°) on treatment with ZnMeI. The acid (I, R=H) boils at 145°/3 mm. (semicarbazone, m.p. 169°). The acid is identical with Semmler and Bartelt's compound.

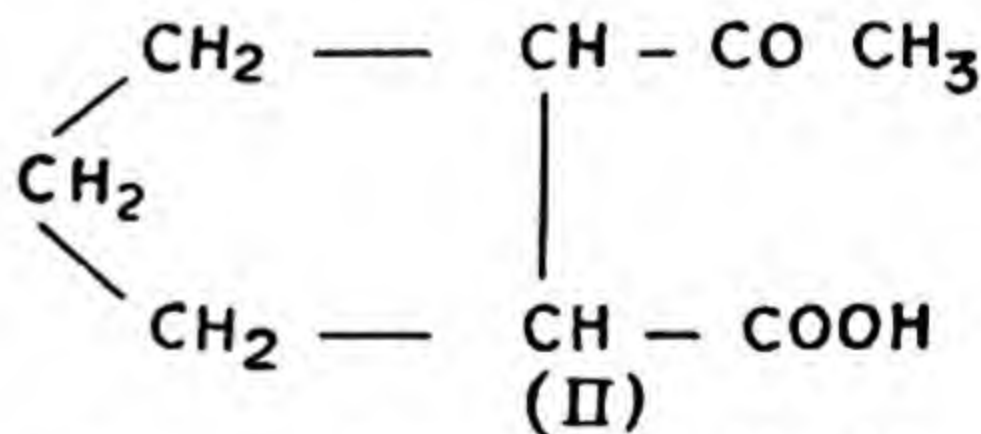
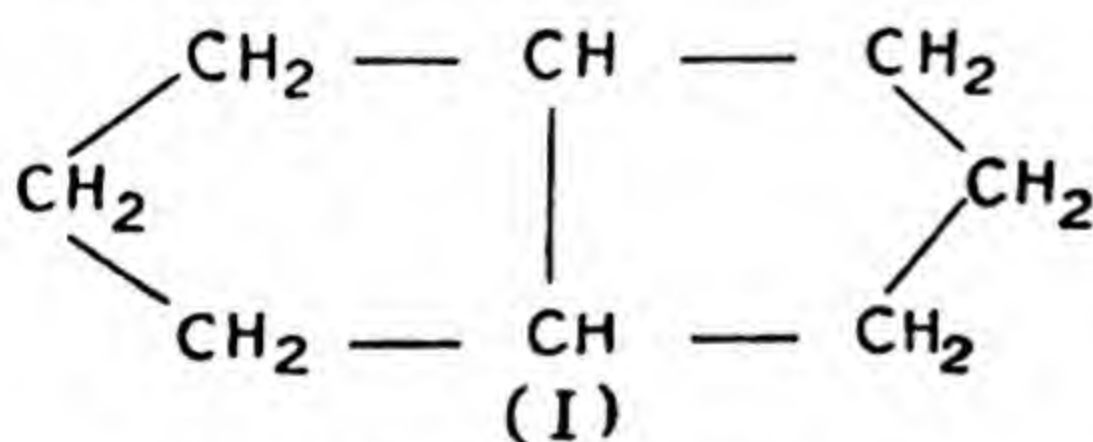
Various experiments were conducted with a view to obtaining the interesting diketone (II) from (I, R=CH<sub>3</sub>). The ester seems to be fairly stable to the action of sodium in benzene or ether solution, but in alcoholic solution, along with the acid (I, R=H) which is the main product, a small amount of the diketone (m.p. 123.5°) is formed which with semicarbazide gives a solid, m.p. 224°.

Experiments are in progress towards obtaining (II) in sufficient amounts to reduce it to homo-norcamphor.

#### 124. Experiments towards the synthesis of bicyclo-(0:3:3)-octane. A synthesis of 1-acetyl-cyclopentane-2-carboxylic acid.

P. C. GUHA and S. K. RANGANATHAN, Bangalore.

With the object of synthesizing derivatives of the bicyclic compound (I), *cis*-1-acetyl-cyclopentane-3-carboxylic acid (II) has been synthesized as follows:



Perkin's pentane-1:1:5:5-tetracarboxylic ester (*J. Chem. Soc.*, 51, 244) was prepared according to the improved method of Guha and Seshadriengar (*Current Science*, 1934, 3, 21), b.p. 196-202°/4 mm. The ester is smoothly cyclized with bromine to give a good yield of the pure ring tetraester, b.p. 175-180°/4 mm. The *ciscyclopentane*-1:2-dicarboxylic anhydride was obtained from this after the method of Perkin. The monoacid monomethyl ester gives the anhydride when distilled; the monoacid chloride boils at 107°/4 mm. The ketonic ester corresponding to acid (II) was obtained from it with ZnMeI (b.p. 94°/3-4 mm.; semicarbazone, m.p. 146°). The acid (II) boils at 142°/3 mm. (semicarbazone, m.p. 176°).

Komppa and Rohrmann's (*Annalen*, 1934, 509, 259) reaction on the anhydride gave only a small amount of a lactone b.p. 143-145°/25 mm. but not the expected ketonic acid (II).

Experiments are in progress to effect ring closure of the ketonic ester corresponding to the acid (II).



## 125. Work on the synthesis of thujane skeleton.

P. C. GUHA and S. K. RANGANATHAN, Bangalore.

*Cis*cyclo propane-1:2-dicarboxylic anhydride has been prepared with a view to converting it into bicyclo-(0:1:3)-hexane-2:4-dione via the ketonic ester (cf. preceding abstracts). Experiments are described showing the action of malonic ester upon the anhydride, with a view to obtaining ultimately bicyclo-(0:1:3)-hexane-4-one.

## 126. Studies in bridge formation: Attempts to synthesize bicyclic terpenes of the thujane group.

P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

All attempts to prepare solid derivative of the bridged ester (cf. 1935, *Sci. Cong., Abstracts* No. 106) proved futile although the unbridged ester gave solid derivatives with hydrazine hydrate (m.p. 156-57°) with phenylhydrazine (m.p. 150°) with aniline (m.p. 262°) and with alcoholic ammonia (m.p. 225°). Controlled hydrolysis of this bridged ester by dilute acids and water under pressure has been studied and the resulting products are being investigated. Reduction of this bridged 2:6-cyclohexanedicarboxylic ester with zinc amalgam is in progress.

*cyclo*Hexanone-2:6-dicarboxylate on hydrolysis with 10% methyl alcoholic potash gives a compound, m.p. 126°. It is soluble in hot alkali but does not come down on cooling or on acidification. It does not give any colouration with ferric chloride.

## 127. Attempts to synthesize bicyclic terpenes of the thujane group.

P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

Ethyl *cyclopentane* tetracarboxylate (1:1, 2:2) has been prepared in a better yield and on being subjected to alcoholic sodium ethoxide treatment gave a liquid b.p. 105-110°/5 mm., a solid m.p. 162-63° (identified as *cyclopentane trans*-1:2-diacid) and another thick viscous undistillable liquid closely resembling the bridged ester described in the preceding paper. These products are being further investigated.

128. *Nor*-caryophyllenic acid.

S. K. RANGANATHAN and N. K. SESHADRIENGAR, Bangalore.

The recent investigations of Ruzicka, Simonsen and others (*Helv., Chim. Acta*, 1935, 18, 219; *J. Chem. Soc.*, 1934, 1806; *ibid.*, 1935, 532; *Chem. and Ind.*, 1935, 54, 151) have shown that *norcaryophyllenic* acid is 1:1-dimethyl-*cyclobutane*-2:3-dicarboxylic acid. A synthesis of this acid is possible by cyclizing 2:2-dimethylbutane-1:1:4:4-tetracarboxylic ester with bromine and subsequent hydrolysis followed by decarboxylation.

Contrary to our expectations, the reaction of *isobutylene* dibromide with malonic ester in alcoholic solution gave ethane tetracarboxylic ester along with some unreacted malonic ester. Heating the magnesium derivative of malonic ester with the halide in alcoholic solution under pressure gave a small amount of a high boiling ester. The rather low yield of this substance, together with the announcement of a successful synthesis of *norcaryophyllenic* acid by Rydon (*Chem. and Ind.*, 1935, 54, 315; *ibid.*, 1935, 54, 559) has made us suspend this investigation.



129. Action of alkylenedihalides on ethyl *cyclopentane-1-one-2 : 5-dicarboxylate*.

P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

The action of ethylene bromide on the disodium and magnesium derivatives of the keto diester is described. The action of other dihalogen compounds is under investigation.

130. Action of alkylenedihalides on ethyl *cyclohexane-1-one-2 : 6-dicarboxylate*.

P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

Experiments are described showing the action of ethylene bromide upon the disodium and magnesium derivatives of *cyclohexanone-2 : 6-dicarboxylic ester*. Investigation on the action of other dihalogen compounds, e.g. methylene iodide, trimethylene bromide, *isobutylene bromide*, etc. are in progress.

131. Action of trimethylene bromide on *acetonedicarboxylic ester* : A new and more convenient method of synthesis of ethyl *cyclo-hexanone-2 : 6-dicarboxylate*.

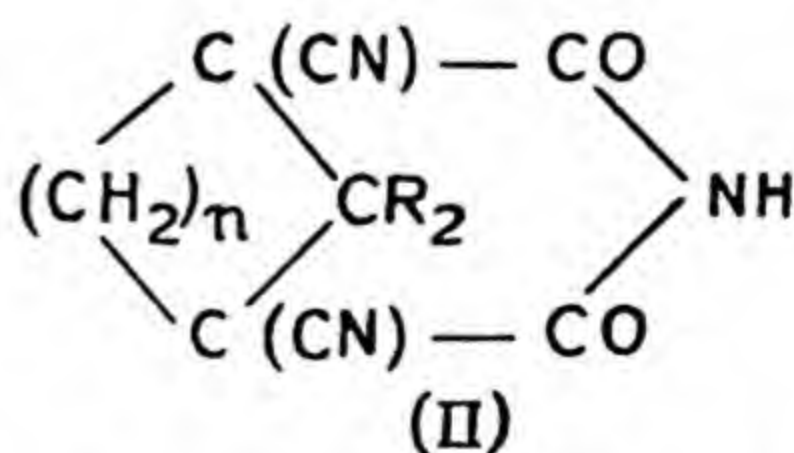
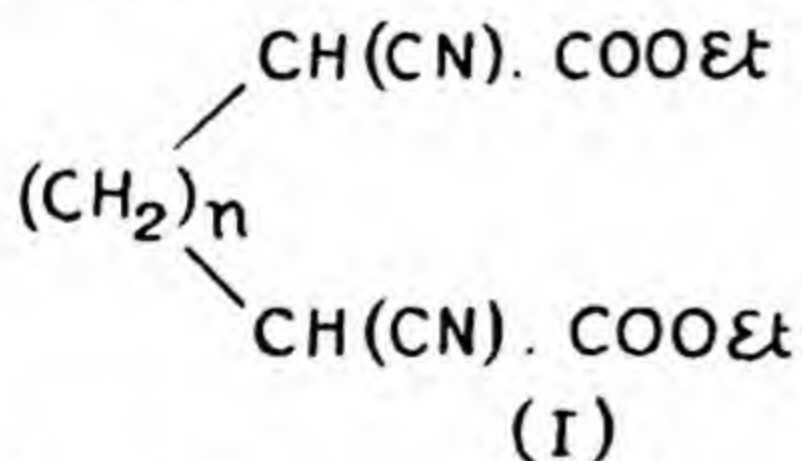
P. C. GUHA and N. K. SESHADRIENGAR, Bangalore.

The reaction of sodium or sodium ethoxide with *acetonedicarboxylic ester* is always attended with the formation of phenolic bodies (Jerdan, *J. Chem. Soc.*, 1887, 71, 1106) and according to Perkin (*J. Chem. Soc.*, 1887, 51, 739 ; cf. 1935 *Sci. Cong. Abstracts* No. 104) of compounds containing oxygen in the ring. Hence, it was considered desirable to try a milder metallic derivative. Trimethylene bromide reacts with the magnesium derivative of *acetonedicarboxylic ester* to yield the expected ethyl *cyclohexanone-2 : 6-dicarboxylate*, b.p. 144°/3 mm., phenylhydrazone m.p. 150°. This new method is more convenient to work with and the yield compares favourably with that obtained by the older method (cf. 1935 *Sci. Cong. Abstracts* No. 106).

132. On the action of ketones and ammonia on alkylene bis-cyanoacetic esters.

P. C. GUHA and S. K. RANGANATHAN, Bangalore.

Guareschi obtained aryl and alkyl substituted dicyanoglutarimides by condensing cyanoacetic ester with ammonia and ketones. The present investigation was undertaken with the object of synthesizing bicyclic compounds of type (II) by the action of ammonia and ketones on alkylene biscyanoacetic esters of type (I).



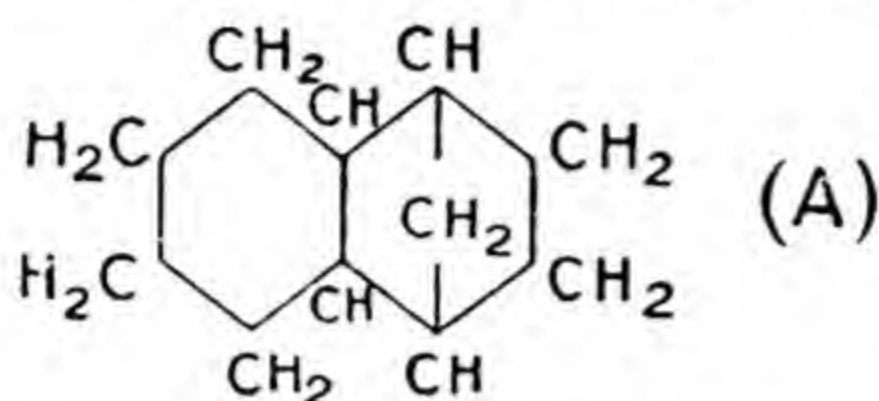
Methylene biscyanoacetic ester could not be obtained according to the method of Higson and Thorpe (*J. Chem. Soc.*, 1906, 89, 1458) though repeated under various conditions for more than a dozen times, but the desired ester has been obtained in poor yield by the action of methylene



iodide on sodiocyanacetic ester, b.p.  $200.5^{\circ}/25$  mm. The above ester (1 mol.) condensed with acetone (1 mol.) in presence of ammonia (3 mols.) to give a yellow crystalline substance, m.p.  $256-59^{\circ}$ . From a cold alkaline solution of this substance on acidification was obtained a colourless crystalline solid, m.p.  $272^{\circ}$  (decomp.). Experiments on the preparation of bicyclic compounds of type (II) starting from ethylene biscyanacetic ester are in progress.

### 133. Synthesis of bridged ring systems.

NRIPENDRANATH CHATTERJI, Calcutta.



The product of the interaction of ethyl sodiocyanoacetate and ethyl  $\Delta^1$ tetrahydrobenzoate readily reacted with ethyl bromoacetate to give ethyl 1-carboxy-cyclohexane-2- $\alpha$ -cyano succinate (b.p.  $200^{\circ}-210^{\circ}/6$  mm.), which on hydrolysis gave 1-carboxy cyclohexane-2-succinic acid (gummy). The ethyl ester (b.p.  $160^{\circ}-170^{\circ}/6$  mm.) of the above acid on condensation with granulated sodium give ethyl (0 : 3 : 4-bicyclo) nonan-2-one-3 : 4-dicarboxylate (b.p.  $173^{\circ}-183^{\circ}/7$  mm.) which on hydrolysis furnished a keto-acid (gummy). The ester of the above keto-acid reacted with ethyl bromoacetate to give ethyl (0 : 3 : 4-bicyclo)-nonan-2-hydroxy-2-acetate-4-carboxylate. It is expected that dehydration and catalytic reduction will give ethyl (0 : 3 : 4 bicyclo)-nonan-2-acetate-4-carboxylate which will undergo ring closure in presence of sodium to yield a keto ester. The above compound (A) may be obtained by the reduction of the ketone that will be obtained after the hydrolysis of the above keto ester.

### 134. Dimethylamino- and diethylamino-phenylimino-camphors—reagents for mercury.

MAHAN SINGH and H. B. DUNNICLIFF, Lahore.

The alcoholic solution (1%) of the dimethyl compound gives a deep scarlet colour with mercurous and mercuric salts. The diethyl compound, however, gives a deep violet colouration with mercurous and mercuric salts. The reagents do not give any indication with Pb, Cu, Cd, Co, Ni, Fe<sup>++</sup>, Fe<sup>+++</sup>, Ca, Ba, Mn (ous) and Mg salts. Bismuth salts give a faint pink coloration along with a small amount of white precipitate.

The spot reaction can be used to detect 1 part of HgNO<sub>3</sub> or HgCl<sub>2</sub> in 50,000 parts of water. A drop of Hg-salt gives a rich pink spot which vanishes on exposure to the vapour of ammonia, but a drop of mercurous nitrate gave a fringe round a white spot. On exposure to ammonia, the spot changed to black. These experiments are being continued.

### 135. Rotary powers of some substituted camphoranilic acids.

MAHAN SINGH and H. B. DUNNICLIFF, Lahore.

The paper describes the rotatory powers of 2'- and 4'-ethyl-, 3'- and 4'-nitro-, 3'- and 4'-amino-, 3'- and 4'-fluoro-, 3'- and 4'-aceto-, and 3'- and 4'-acetylamino-camphoranilic acids. The effect of fluorine is in agreement with that of other halogen atoms. The amino- and aceto-groups in the *para* position produce an exaltation in the rotatory power.



## 136. Condensations of furil and furoin.

A. C. SIRCAR and S. C. GUHA, Calcutta.

Benzil and benzoin are very well adapted for various types of condensations (Japp and Hooker, *J. Chem. Soc.*, 1884, T, 672; Japp and Robinson, *ibid.*, 1882, T, 326; Anschütz and Geldermann, *ibid.*, 1891, Abs. 725; Japp and Murray, *ibid.*, 1894, T, 889; Japp and Meldrum, *ibid.*, 1899, T, 1037, etc.). Many of these condensation products are very interesting both from the theoretical as well as practical point of view. It was therefore expected that the heterocyclic compounds furil and furoin would also yield a series of similar condensation products. In the present paper a large number of such condensation products have been described.

## 137. Velocity of transformation of 1 : 3 : 5-triketones into 2 : 6-disubstituted 4-pyrones.

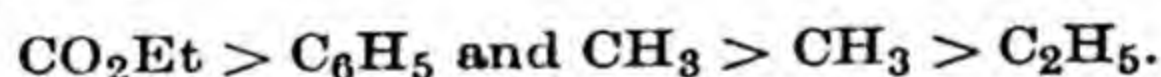
C. W. GUBNIS, W. B. BHAGBAT, and S. S. DESHAPANDE, Indore.

The transformation of 1 : 3 : 5-triketone such as diacetylacetone into dimethylpyrone with loss of water is supposed to be due to the dehydrating action of the solvent in which the reaction takes place. The authors, however, find that no such dehydrating conditions are necessary and that a triketone changes spontaneously into its pyrone in non-dehydrating solvents in the presence of a catalyzer. The velocity of this change is measured and the reaction is found to be strictly unimolecular. Since the total change is the result of these changes, namely (a) tautomeric interchange between the keto and dienolic forms of the triketone, and (b) conversion of the dienol into pyrone, the equation

$$\frac{1}{t} \log \frac{a}{a-x} = k \frac{m}{1+m}$$

is derived on assumption that change (a) is rapid and reversible while (b) is slow and non-reversible.

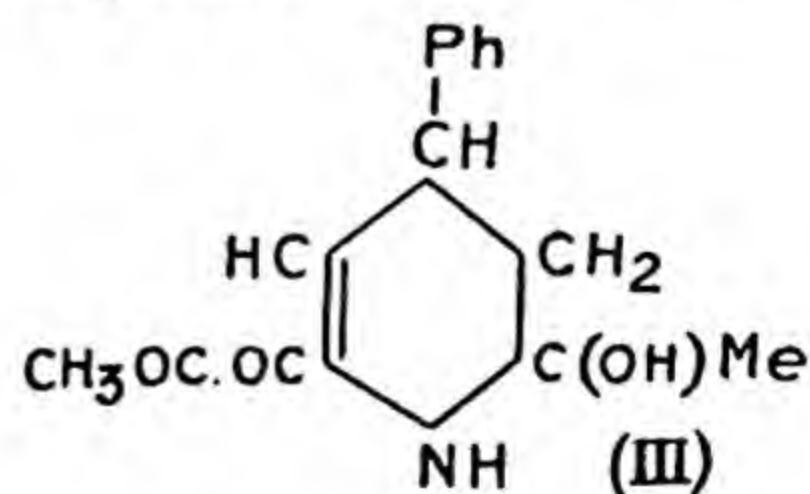
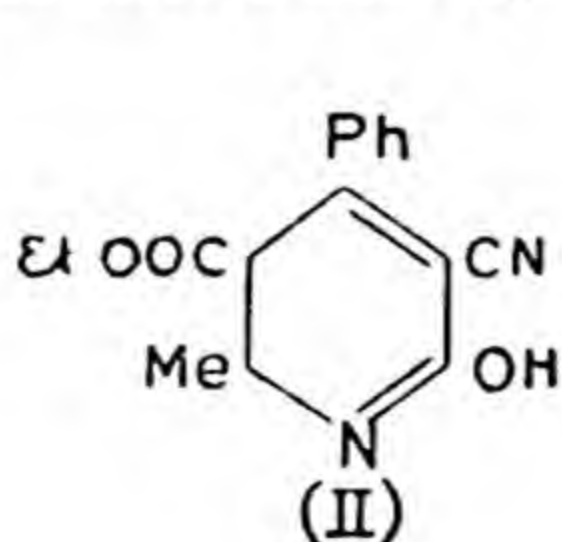
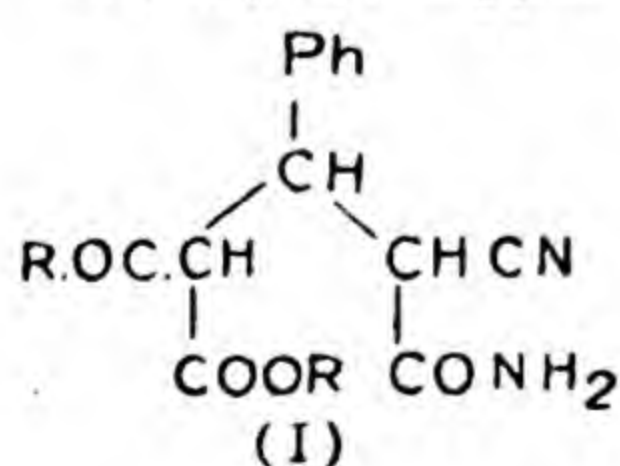
The study of transformation of acetone dioxalic ester, diacetylacetone, dipropionylacetone and benzoylacetyl acetone has shown the effect of the groups carbethoxy, methyl, etc. on the velocity constant of the reaction. The groups arranged in the decreasing order of their effects are



## 138. A modification of Guareschi's synthesis for pyridine derivatives.

NIRMALANANDA PALIT, Patna.

From the product of the action of ammonia on benzaldehyde, acetoacetic ester and cyanacetic ester, Guareschi isolated a compound, m.p. 222-3° (*Zentr.*, 1897, 927-28). In a later work (*ibid.*, 1907, i, 332) he described the reaction product as a mixture from which one compound (m.p. 225-26°) was definitely characterized as (I), while a second (m.p. 226-7°) was supposed to be derived from (I) and regarded as (II).





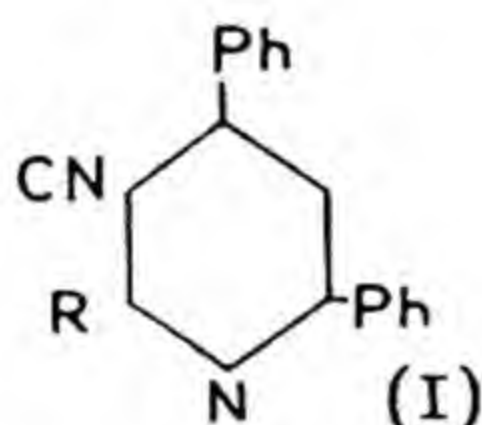
To throw further light on the products of this reaction, it was thought advisable to couple the four reactants in pairs and to treat the resulting benzylidene-acetoacetic ester and cyanacetamide with a more suitable condensing agent. Thus with diethylamine, only one condensation product, m.p. 222-23°, results in 68% yield. Analysis showed it to be an addition product, but its properties could not be reconciled to structure (I), for it did not evolve any ammonia with boiling caustic soda, but dissolved to be reprecipitated with acids. Boiling dil. HCl hydrolyzes it to phenyl-acetylbutyric acid. The substance is probably represented by the cyclic aldol structure derived from (I) (Barat, *J. Indian Chem. Soc.*, 7, 322). Boiling acetic anhydride instead of producing Guareschi's compound (II) brings about an abnormal change yielding (III) (Allen and Scarrow, *Zentr.*, 1935, I, 1869). Further work is in progress to elucidate its constitution.

The reaction has been further extended to dinitriles and it has been found that benzoacetodinitrile and *p*-anisylacetodinitrile give the proper hydroxypyridine derivative corresponding to II, but *p*-toluacetodinitrile yields again the abnormal addition product with cyclic aldo structure.

### 139. Gastaldi's synthesis of pyridines from pyrylium salts.

NIRMALANANDA PALIT, Patna.

Gastaldi (*Gazzetta.*, 1922, i, 169, 305) has thrown considerable doubt upon the constitution of the products of pyridine derivatives synthesized by Meyer (*J. pr. Chem.*, 1908, 78, 497) by condensing dinitriles with arylidene ketones, in view of the fact that 2 : 4-diphenyl-6-methylpyridine prepared by him (Gastaldi) from the corresponding pyrylium salt was found to be different from the product obtained by Meyer by hydrolysis and decarboxylation of (I)



In order to clear up this controversy, the synthesis of 2 : 4-diphenyl-6-methylpyridine was attempted by condensing  $\beta$ -aminocrotonic ester with dibenzoylmethane without success. The condensation of styryl-phenylketone with acetoacetic ester according to Knoevenagel (*Ber.*, 35, 397), and treatment of the resulting 1 : 5-diketone with  $\text{NH}_3$  or hydroxylamine to close up the ring, also met with failure. Under different experimental conditions, the 1 : 5-diketone exists in two stereoisomeric forms.

The corresponding 2 : 4 : 6-triphenyl derivative was easily obtained by Meyer's reaction by condensing benzoacetodinitrile with O-ethylether of dibenzoylmethane, followed by hydrolysis and decarboxylation, and was found to be identical with the compound obtained by Newmann (*Annalen.*, 302, 240) by an entirely different method, thereby proving the validity of Meyer's mode of representation.

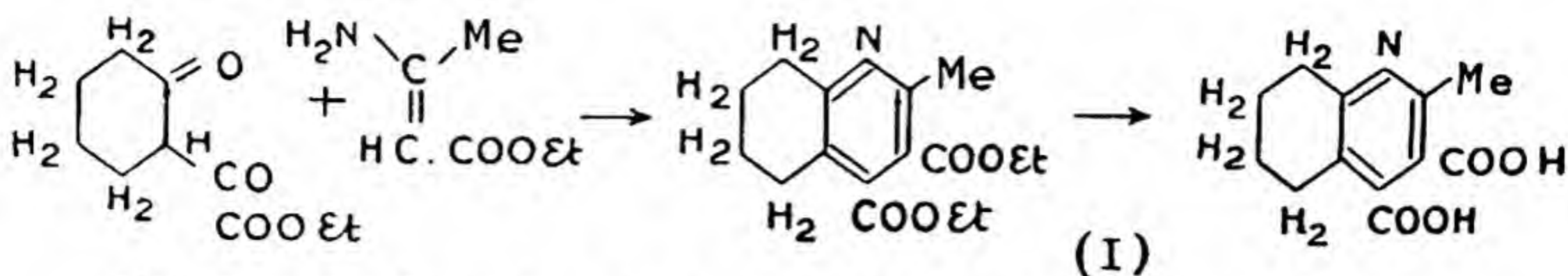
### 140. On the synthesis of Bz-tetrahydro-cinchoninic acid.

UMAPRASANNA BASU, Calcutta.

The present work has been undertaken with the intention of synthesizing a Bz-tetrahydro-cinchoninic acid which would be required for another purpose. Up till now a dicarboxylic acid (I) has been obtained by hydrolyzing with a caustic potash solution (15%), the condensation



product formed by simply mixing ethyl  $\beta$ -aminocrotonate with cyclohexanone-2-oxalate thus :



The first condensation product, ethyl 2-methyl-Bz-tetrahydro-quinoline-3 : 4-dicarboxylate, is a refracting yellow liquid, b.p. 191°/5 mm. This on hydrolysis gave the acid (I) as a crystalline solid, m.p. 272-73° with decomposition. Further work is in progress.

#### 141. Synthesis of quinoline derivatives.

T. N. GHOSH, Bangalore.

It has been shown in a previous communication (Ghosh, *J. Indian Chem. Soc.*, 1934, 11, 27) that *o*-nitrobenzal-phenylthiohydantoin, on reduction, yields a quinoline derivative. The reaction has now been extended with other thiohydantoin derivatives and phenylhydantoin. The quinoline derivatives, so obtained, have similarity in structure to glyoxalinquinolines (Narang and Ray, *J. Chem. Soc.*, 1931, 976) which possess antimalarial properties.

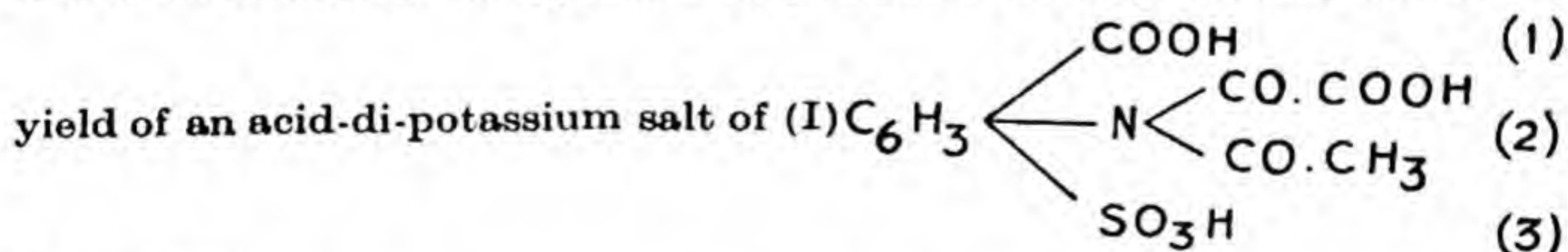
Dicarbethoxythioacetylcarbamic acid reacts with hydrazine hydrate to form a pyrazolone derivative yielding, on hydrolysis, 3-carboxyiminopyrazolone. The latter compound containing a reactive methylene group, reacts with *o*-nitrobenzaldehyde, and the resulting product, on reduction, yields a quinoline derivative with fused pyrazolone ring. Antipyretic properties of this compound will be studied later on. Work on the synthesis of similar quinoline derivatives from pyrazolones, obtained by the method of Worrall (*J. Amer. Chem. Soc.*, 1923, 45, 3092) is in progress.

#### 142. Oxidation of quinoline-sulphonic acids.

K. V. BOKIL, Ahmedabad.

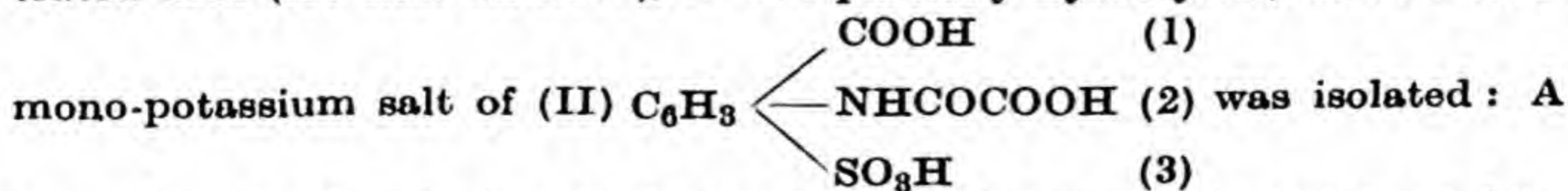
Oxidation of quinoline-8-sulphonic acid with alkaline KMnO<sub>4</sub> gives, along with quinolinic acid, only a very small quantity of 2-amino-3-sulphobenzoic acid (Zürcher, *Ber.*, 1888, 21, 180).

If, however, quinoline-8-sulphonic acid is first reduced, acetylated and then oxidized, the pyridine ring is preferentially broken, and a 65%



is obtained.

Attempts to hydrolyze this with either concentrated aqueous or alcoholic KOH have been so far unsuccessful. When boiled with concentrated HCl (for half an hour), it was partially hydrolyzed, and an acid-



small part is also further hydrolyzed with the formation of free amino-



sulpho-benzoic acid, since (1) the aqueous solution gives the characteristic blue fluorescence, and (2) a small quantity of oxalic acid formed, is recovered. If boiling with HCl is continued for a longer period, the substance (II) is completely decomposed.

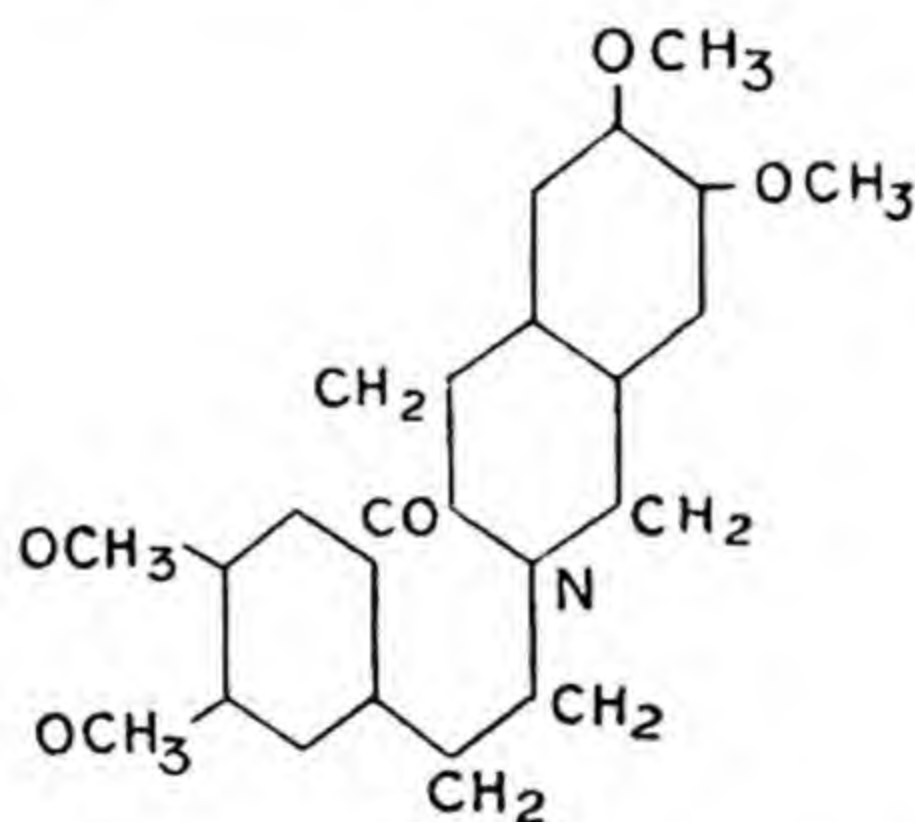
A similar oxidation of acetyl-tetrahydro-5-quinoline-sulphonic acid is under investigation.

### 143. On some isoquinoline compounds.

P. K. PAUL, Calcutta.

With a view to building up some isoquinoline skeleton, having in the main that present in emetine, the present piece of preliminary work has been undertaken with the following results.

Homoveratric acid has been condensed with formaldehyde and the resulting lactone (m.p.  $100^{\circ}$ ) has been condensed with  $\beta$ -veratryl-ethylamine, giving rise to a substance (m.p.  $123^{\circ}$ ) of the following constitution.



The suitable condition for its ring closure into the corresponding isoquinoline derivative is being studied.

### 144. Experiments on the synthesis of alkaloids belonging to chelidonine-chelerythrine group. Part I. Synthesis of $\alpha$ -naphthaphenanthridine, the parent substance of the group.

S. N. CHAKRAVARTI and M. SWAMINATHAN, Annamalainagar.

A general method has been worked out by one of us (S. N. C.) for synthesizing the alkaloids belonging to chelidonine-chelerythrine group. In a series of preliminary exploratory experiments, we first attempted the synthesis of  $\alpha$ -naphthaphenanthridine in the following manner:—

$\beta$ -Benzoyl- $\alpha$ -phenylpropionic acid, prepared according to the directions of Lapworth, was first reduced to  $\alpha\gamma$ -diphenylbutyric acid, and the latter cyclized to 1-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p.  $75^{\circ}$  by means of concentrated sulphuric acid. The oxime, m.p.  $169^{\circ}$ , of the ketone was reduced to 1-amino-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene and attempts made to effect the ring closure of the formyl and acetyl derivative of the latter to a compound of the type of  $\alpha$ -naphthaphenanthridine.



## 145. Vasicine.

J. N. RAY, Lahore.

A review of the literature of vasicine.

The constitution of dehydroacetyl-vasicine and the oxidation products with hydrogen peroxide are discussed. An alternative synthesis of vasicine is also described.

## 146. Experiments on the synthesis of yohimbine. Part I. Yobyryne.

J. N. RAY, Lahore.

$\beta$ -Indyl-ethylamine is converted into tetrahydro- $\beta$ -carboline. The N-O-cyanobenzyl derivative is converted to an aldehyde by Stephen's reaction. Cyclization leads to yobyryne also obtained from yohimbine by selenium dehydrogenation.

## 147. Studies in the anthraquinone series.

P. C. MITTER and MISS TANIMA SEN-GUPTA, Calcutta.

In attempting to prepare anthraquinone-carboxylic acids of the morindone type, we oxidized 1-acetoxy-2-methoxy-6-methyl-anthraquinone with chromic acid and on deacetylating the product, obtained 1-hydroxy-2-methoxy-anthraquinone-6-carboxylic acid, m.p. 195°.

Next, opianic acid was condensed with methyl 5-bromo-salicylate, in presence of sulphuric acid when 5:6-dimethoxy-2-(2'-hydroxy-3'-carbomethoxy-6'-bromophenyl) phthalide, m.p. 215° was obtained. On hydrolysis it gave the corresponding acid, m.p. 253°. Reduction of the phthalide with zinc dust and caustic soda gave 5:6-dimethoxy-2-(2'-hydroxy-3'-carboxybenzyl) benzoic acid, m.p. 225°. Neither the acid nor its bromo-derivative could be converted into the corresponding anthrone.

## 148. Dyes of the triamino-triphenyl-methane series.

K. S. VENKAT RAMAN, Benares.

*p*-Dimethylaminobenzaldehyde has been condensed with two molecules of methyl-aniline, ethyl-aniline, diethyl-aniline, methylbenzyl-aniline, benzyl-aniline, *o*-toluidine, *p*-toluidine, etc. in presence of concentrated HCl, to yield dyes of the crystal violet type. The leuco bases thus obtained are very easily oxidized, undergoing slow oxidation even on exposure. The leuco bases of the crystal violet series seem to get oxidized much more easily than the members of the malachite green series. The dyes obtained from these compounds range in colour between bluish violet to violet.

## 149. Dyes derived from acenaphthenequinone. Part V. 2-(6-methyl) thionaphthene-acenaphthylene-indigos.

S. K. GUHA, Patna.

In continuation of parts III and IV in this series (Guha, *J. Indian Chem. Soc.*, 1932, 9, 423; *ibid.*, 1933, 10, 679), this investigation was undertaken to prepare vat dyes from acenaphthenequinone and its various derivatives and 6-methyl-3-hydroxy-thionaphthene (D.R.P. Nr 204763; Friedlander, 9, 589; Auwers and Thies, *Ber.*, 1920, 53, 2293) with a view to examining the effect, if any, produced on the colour of ciba Scarlet G (Bezdzik and Friedländer, *Monatsh.*, 1908, 29, 386; E.P. 344/08) by the introduction of CH<sub>3</sub>-group in the 6-position of the thionaphthene nucleus, and how far this effect can be compared with 2-(5-methyl) thio-



naphthene-acenaphthylene-indigos (Guha, *loc. cit.*) which were found to be deeper in colour than ciba Scarlet G and its halogen derivatives (Mayer and Schönfelder, *Ber.*, 1922, 55, 2972 ; Guha, *loc. cit.*).

150. The condensation of 5 : 5-dimethyldihydroresorcin with aromatic amines.

B. H. IYER, Bangalore.

According to Paul Haas (*J. Chem. Soc.*, 1906, 89, 202, 394) when one molecule of an amine reacts with one molecule of dimethyldihydroresorcin, the remaining keto-group gets enolized. With a view to studying the nature of keto-enol tautomerism present in methone, detailed observations regarding its behaviour towards aromatic amines, on condensation as also on diazotization and coupling, are being made. It has been successfully condensed with benzidine and *o*-tolidine. In molecular proportions and by allowing the reaction to proceed for a short period, the acid soluble mono-methonyl-benzidine (m.p.  $219^{\circ}$ ) and mono-methonyltolidine (m.p.  $254^{\circ}$ ) are formed. These give coloration with ferric chloride and yield acetyl derivatives. In presence of excess of methone and on prolonged heating, dimethonyl-benzidine (m.p.  $395^{\circ}$  decomp.) and dimethonyl tolidine (m.p.  $320^{\circ}$  decomp.) are formed.

By coupling methone with tetrazotized benzidine and tolidine, the corresponding azo-dyes have been prepared.

*Para*-nitraniline could not be condensed with methone but the corresponding azo-compound has been prepared.

151. The phytosteryl acetate test for detection of hydrogenated fats in ghee.

K. N. BAGCHI and N. S. MAZUMDAR, Patna.

The phytosterol acetate test for detecting vegetable fats in ghee becomes unreliable when applied to mixtures of ghee and hydrogenated fats (vegetable ghee), owing to conversion of the phytosterol into resinous hydrocarbons during hydrogenation at high temperatures ( $250^{\circ}$ ).

The following observations may therefore be helpful to detect hydrogenated fats in ghee by this method : (1) Formation of brown resinous droplets on cooling a hot alcoholic solution of the resaponified sample or its ether extract. (2) Under the microscope the typical cholesterol crystals partially covered with the amorphous deposit are seen but no phytosterol crystals. (3) On acetylation of the ether extract (sterols with other unsaponifiable matter), the resinous substance forms a sticky brown coating in the basin—cannot be detected. (4) After acetylation the residue (Sterol acetates and hydrocarbons) dissolved in alcohol and allowed to crystallize. Filtered crystals set aside for determination of melting point and the filtrate evaporated to dryness. The melting point of the dry residue, which is a mixture containing the resinous substance, original hydrocarbons and varying amount of cholesterol, is always low—varying from  $50^{\circ}$  to  $70^{\circ}$ . In pure ghee the residue is a pale yellow liquid.

In one and the same experiment the presence of both the unhydrogenated and hydrogenated oils is detected. Digitonin method is not to be adopted for these observations.

152. The constituents of the seeds of *Corchorus olitorius*, Linn.

N. K. SEN, Dacca.

The seeds of *Corchorus olitorius*, a second variety of Jute-seeds, largely used in fever and dysentery, have been the subject-matter of an investigation.



Petroleum ether extract yields a clear tasteless pale yellow oil whose physical and chemical characteristics have been determined. The total fatty acids have been separated into saturated and unsaturated acids by Twitchell's method. The unsaponifiable matter yields a phytosterol of m.p.  $130^{\circ}$  and a small quantity of higher alcohol of the aliphatic series. Ether and chloroform extracts give some resin and oily matter. Alcohol extract yields (i) a quantity of sugar, (ii) colouring matter and resinous matter from which is isolated a non-alkaloidal bitter substance. It is found to be a glucoside of corchorin-group described by the author in previous communications.

153. Studies in cashewnut shell oil.

N. M. PATEL and M. S. PATEL, Bombay.

Continuing previous work, the extracted oil was heated at  $100^{\circ}$ ,  $125^{\circ}$ ,  $150^{\circ}$ ,  $175^{\circ}$ , and  $200^{\circ}$  in an atmosphere of nitrogen, and in sealed tubes. The physical and chemical constants of the samples obtained by the above treatment have been determined. Mean molecular weights of the same have also been determined by cryoscopic method. The carbon dioxide evolved during heating at various temperatures has been determined. On prolonged heating the oil solidifies and is not affected by alkali, acids, alcohol, and similar other solvents. The oil does not dry nor absorb any oxygen when kept in an atmosphere of oxygen for a considerable length of time both at ordinary or higher temperatures. All attempts to decolourize the oil have been unsuccessful.

The bromo-compound has been separated and analyzed; it throws some light on the constitution of the oil. The acetylated product has been studied as to its drying properties.

The oil distils with decomposition giving a light coloured phenolic substance and turning dark on standing a tarry material as residue. The chemical constants and mean mol. wt. of this have been determined. The properties of the tarry material have been studied.

The physical and chemical constants of the oil extracted from roasted cashewnut shells discarded by cashewnut factories have been determined, and the roasted shells subjected to destructive distillation, the products of which have been examined. The shells yield only 1.7% ash, consisting mostly of  $\text{Na}_2\text{CO}_3$  and  $\text{MgO}$ . Further work is in progress.

154. The chemistry of indigenous fatty oils. Part XI. The chemical composition of the fat from the seeds of *Garcinia indica*.

P. RAMASWAMI AYYAR and MISS P. DEVI, Bangalore.

The analytical characteristics of the fat forming 53 per cent. of the seeds have been determined. The fatty acids have been separated into saturated acids (68.7 per cent.) and liquid acids (31.3 per cent.); the former consisting preponderantly of stearic acid. The latter on oxidation has yielded an isomeric dihydroxy-stearic acid, m.p.  $95-96^{\circ}$ , in addition to the more common variety, m.p.  $131-32^{\circ}$ , and azelaic acid, m.p.  $104-5^{\circ}$ . The nature of the isomeric oleic acid present is being investigated.

155. Isolation of a new constituent from the unsaponifiable matter of the oil of *Pongamia Glabra*.

B. L. MANJUNATH and S. SIDDAPPA, Bangalore.

During the investigation of the unsaponifiable matter from the oil of *Pongamia Glabra*, Karengin was removed by extraction with methyl alcohol and an amorphous white material was obtained as the residue. This was found to be insoluble in most of the usual organic solvents.



However, it dissolved in glacial acetic acid and was reprecipitated on dilution with water. The product could then be crystallized from methyl alcohol when it separated in clusters of white needles, m.p.  $75^{\circ}$ . It has the formula  $C_{11}H_{22}O$  and does not contain either a hydroxyl or carbonyl function. The paper deals with the structure of this compound provisionally named *Pongamin*.

156. The isomerism of higher unsaturated fatty acids and their derivatives. Part IV. The nature of the oleic acid occurring in the fatty oil from the seeds of *Adenanthera pavonina*.

P. RAMASWAMI AYYAR and M. T. CHOBE, Bangalore.

The occurrence of  $\Delta^{9:10}$  oleic acid in the liquid acids of this oil has been confirmed by the formation of the characteristic dihydroxy stearic acid, m.p.  $131-32^{\circ}$ , and of azelaic acid, m.p.  $104-5^{\circ}$ .

157. The chemical examination of the essential oil from *Lansium annamalayana* (Bedd).

H. S. JOIS, B. L. MANJUNATH, and D. VENKATARAMIAH, Bangalore.

The essential oil obtained by the steam distillation of the wood of *Lansium annamalayana* was found to have the following constants:  $d_{20}^{25}$ , 0.8952;  $n_D^{25}$ , 1.4950;  $[\alpha]_D^{25}$ ,  $-62.3^{\circ}$ ; acid value, 0.5; ester value, 0.6; ester value after acetylation, 22.7. A detailed study of the oil has shown that it consists of a new sesquiterpene (about 90 per cent.), *Lansene* (b.p.,  $98-101^{\circ}/0.5$  mm.;  $d_{20}^{25}$ , 0.8915;  $n_D^{25}$ , 1.4943;  $[\alpha]_D^{25}$ ,  $-62.38$ ; dihydrochloride, b.p.  $140-142^{\circ}/0.5$  mm.) and a new sesquiterpene alcohol, *Lansol* (b.p.  $130-132^{\circ}/0.5$  mm.;  $d_{20}^{25}$ , 1.5070;  $[\alpha]_D^{25}$ ,  $-22.0^{\circ}$ ).

A study of the chemistry of these compounds is under investigation.

158. Essential oil of *Blumea eriantha*.

V. C. AMIN and M. S. PATEL, Bombay.

*Blumea eriantha* is one of the most common weeds in the Bombay Presidency. It has been well-known that this plant yields essential oil possessing camphor-like odour. *Blumea* plants grown in Bombay were collected and distilled. The plants on distillation yielded oil with the following constants:—

Specific gravity at  $31^{\circ}$ —0.9290, Acid value—0.86, Saponification value—34.5, Ester value—33.6, Boiling point— $224^{\circ}$ .

Work on the constitution of the oil is in progress.

Samples of oil have been sent to Germany and the U.K. for evaluation. If the price offered compares favourably with the cost of production, the distillation of *Blumea eriantha* is likely to be a good small scale village industry in some parts of the Bombay Presidency.

159. Essential oil from the rhizomes of *Cyperus rotundus*, Linn.

B. J. HEGDE and B. SANJIVA RAO, Bangalore.

The oil has been obtained in an yield of 0.5 per cent., and found to consist mainly of two bicyclic sesquiterpenes, a secondary alcohol  $C_{15}H_{26}O$  and a ketone  $C_{15}H_{22}O$ .



## 160. Studies in plant colouring matters ; Morellin.

B. SANJIVA RAO and K. S. SUBRAMANIAN, Bangalore.

A crystalline mono-guanyl hydrazone ( $C_{31}H_{37}O_7N_5$ ; m.p.  $206^\circ$ ; ( $\alpha_D$ ,  $-748^\circ$ ) of morellin ( $\alpha_D$ ,  $-594^\circ$ ) has been prepared, only one of the two keto-groups reacting with the reagent. On fusion of morellin with potash, acetic acid, mainly isovaleric acid, a dicarboxylic acid ( $C_9H_{10}O_4$ ; m.p.  $176^\circ$ ), optically inactive methyl-heptenol, a ditertiary glycol ( $C_{16}H_{28}O_2$ ) having a strong odour of amyl alcohol, and 1 : 3 : 5-xyleneol have been obtained. The glycol and the solid acid are being further investigated.

161. A note on the essential oil from the rhizomes of *Rheum emodi*, Wall.

M. GHOUSE MOHIUDDIN, Bangalore.

The volatile oil obtained from the alcoholic extract (yield 0.05 per cent.) has been examined. It is composed of eugenol whose odour is characteristic of the drug and a secondary alcohol which is probably methyl-*n*-heptyl alcohol.

## 162. Preparation of starches from jowar and cassawa.

H. P. DAS GUPTA, Bangalore.

Jowar (*Sorghum vulgare*) is steeped in sulphurous acid (1 per cent. approximately) for 4 days and ground to form a homogeneous pulp. This is screened through a 90 mesh sieve and the suspension is allowed to settle overnight, when two distinct layers separate. The bottom layer is directly treated with dilute alkali solution while the top one is first freed from fat and protein by centrifuging and then treated with strong alkali. Starch is then recovered by lixiviation and settling; yield 57 lbs. of starch (95.5% pure) and 20 lbs. of fodder of high nutritive value from 100 lbs. of grains.

Fresh Cassawa tubers (*Manihot aipi*) are cut into small chips and then ground with water to form a pulp. The cellulosic materials are separated by passing through a fine sieve. The milky fluid is allowed to settle and the supernatant liquid syphoned off. The crude starch is then purified by treatment with dilute alkali and recovered by lixiviation and centrifuging; yield about 21 per cent. starch (96 per cent. pure) on the weight of tubers. The residue can be used as fodder of low nutritive value. The viscosity of the starch gel approaches very nearly to that of commercial potato starch.

## 163. On the preparation and properties of some of the degradation products of starch.

H. P. DAS GUPTA, Bangalore.

Starch prepared from different sources was subjected to varying degrees of acid-alcoholic hydrolysis. A number of degradation products were thus obtained, depending upon the time and the nature of acid employed. A comparative flow of the gels prepared from the samples, as also the tint developed by adding dilute iodine solution, were studied respectively by Ostwald's viscometer and Lovibond tintometer. A parallelism between the two sets of readings has been noted. These tintometer readings give greater support to the nature of the degradation products of starch, than does a simple viscosity reading alone.



164. Investigations on the acid contents of kokam, *Garcinia indica*.

A. A. KHAN and K. C. PANDYA, Agra.

In an investigation on the acid content of *Garcinia gambogia*, known in Malayalam as 'Kadumpuli' and in Bombay as 'Vilayati Imli', it was found that the dried rind of the fruit contained 10% tartaric acid, very much like tamarind itself (*J. Indian Chem. Soc.*, 1931, 8, 469). *Garcinia indica* is very much used in the west and central India, and preferred to tamarind as an acid element. An analysis of the dried and salted fruit shows that in this case all the acid is malic acid, about 10%, but there is no tartaric acid. The ash contained phosphates, carbonates, potassium, calcium, iron, and possibly sodium.

165. Investigations on āmchur, the peeled dried unripe mango fruit, *Mangifera indica*.

K. C. PANDYA and R. K. BOUNTRA, Agra.

The dried unripe mango fruit takes the place of kok ām of the west and tamarind of the south and south-west, in the north, particularly in the United Provinces. It is known as Amchur or merely Khatai. It is found to contain tartaric acid (about 6%), citric acid (about 4%), and oxalic acid (about 1%). The ash shows the presence of phosphate, iron, aluminium, calcium, magnesium, potassium, and sodium.

Investigations of other plant-products used as souring elements of our diet are in progress.

166. Manufacture of tannic acid from myrobolans.

S. R. SUNTHANKAR and S. K. K. JATKAR, Bangalore.

By treating myrobolan extract with alumina more of tannins were removed than non-tannins, although the colour of the product was quite satisfactory. Fractional precipitation with increasing quantities of 10 per cent. lead acetate solution and decomposition with sulphuric acid showed that the ratio of tannins to non-tannins is approximately the same in all but the first precipitate. Extraction with a battery of six vats shows that most of the tannins are extracted by water at 70°, about seven times the quantity of myrobolan. Cooling the extract to 10° caused the separation of a good deal of colloidal matter without appreciable loss of tannins. The extract on evaporation and drying in vacuum was found to be equal to commercial tannic acid in dyeing operations.

167. Chemical investigation of an acid isolated from *Ananas sativa*.

P. K. BOSE and S. BHATTACHARYA, Calcutta.

A crystalline acid has been isolated by Dr. B. C. Guha. It has the composition,  $C_8H_{12}O_9$ , m.p. 130–132°. It does not reduce Fehling's or ammoniacal silver nitrate solutions. It does not give any colour reaction with alkaline *o*-dinitrobenzene (Bose, *Z. anal. Chem.*, 1932, 87, 110) even after hydrolysis with acids or alkalies. This proves the absence of -CO-CHOH- group in the acid or in the hydrolyzed products. It does not char with conc.  $H_2SO_4$  (hot). It is optically inactive and gave no colour with neutral ferric chloride solution. Potentiometric titration indicated the presence of one -CO<sub>2</sub>H group and the equivalent weight was found to be 250. On boiling with dilute alkali (excess) it was apparently converted into a tribasic acid. With diazomethane it gave a crystalline compound, m.p. 73–74°, presumably the methyl ester, which



distilled unchanged at 85–90°/0.1 mm. The acid on distillation at 140–45°/0.03 mm. was converted into a neutral body,  $C_8H_{10}O_8$ , m.p. 121–23°, the aqueous solution of which was very stable. The acid is believed to be the anhydride of a saturated tribasic acid or a dilactonic acid.

#### 168. On oroxylin.

P. K. BOSE and S. BANNERJEE, Calcutta.

Oroxylin,  $C_{19}H_{14}O_6$ , m.p. indefinite above 225°, was isolated from *Oroxylum indicum* by Naylor and Dyer (*J. Chem. Soc.*, 1901, 79, 954) in a yield of 0.2%. They obtained phloroglucinol, and benzoic acid, as degradation products. On oxidation phthalic acid was obtained. By a modified method we have obtained 2.8% of crude product from which three crystalline compounds have been isolated, viz. (i) brownish yellow, m.p. 262–67° (yield 0.5%) which agreed in properties with Naylor and Dyer's oroxylin; (ii) bright yellow, m.p. 235–37° (yield 0.8%); (iii) bright yellow needles, m.p. 212–15° (yield 0.1%). Both (i) and (ii) formed acetyl derivatives which are easily hydrolyzed to the parent compounds. They are not anthraquinone derivatives. (i) gives an orange red precipitate with acidified lead acetate and is unstable towards alkalis. (ii) is stable towards alkalis and does not form any salt with acidified lead solutions. On treatment with diazomethane (i) is converted into a yellow crystalline substance, m.p. 235–37°, not identical with (ii).

#### 169. Chemical examination of the fruits of *Solanum nigrum*.

##### Part I. Its constituents.

G. P. PENDSE and N. GHATAK, Gwalior.

20 kg. of the fruits of this highly medicinal plant have been extracted with various solvents. The extracts are under systematic examination. A pale yellow, semi-drying oil to the extent of about 10% of the dried seeds of the fruits has been obtained. The juice is under examination for its alkaloidal contents and also estimation of its organic acids. The husk and the seeds after the oil has been extracted off have been exhaustively extracted with alcohol. The alcoholic extracts of both are under further examination.

#### 170. Chemical examination of the fruits of *Solanum nigrum*.

##### Part II. Constitution of the oil.

G. P. PENDSE and N. GHATAK, Gwalior.

The oil from the fruits of the above plant is under examination. Its physical and chemical constants have been determined and the chemical constitution of the oil is being investigated.

#### 171. Chemical and pharmacological study of *Randia dumetorium* (Sanskrit and Madana : *Deccani-Mendphal* ; English : emetic nut).

S. W. HARDIKAR and M. G. MOHIUDDIN, Hyderabad-Deccan.

The pulp which is reputed to be a good substitute for *Ipecacuanha* was found to contain an acid-saponin (about 35%), a neutral saponin (about 0.5%), an essential oil about (0.1%), a volatile fatty acid, a brown resin (about 2%), and a green colouring matter.

The acid-saponin is soluble in water, insoluble in absolute alcohol (but soluble in 75% alcohol), ether, chloroform, petroleum ether, and benzene. Its melting point is between 245° and 250°. It is hydrolyzed



by acids, saliva and emulsin, yielding glucose, a pentose, and a sapogenin, melting at 124-25°.

Further chemical investigation and pharmacological experiments are in progress.

172. On anacardic acid. Part III.

P. P. PILLAY, Bangalore.

Tetrahydroanacardic acid has been proved to be 6-pentadecylsalicylic acid (*J. Indian Chem. Soc.*, 1935, 12, 226, 231). Since this is quite a new type of acid to be found in nature, its reactions have been studied and several compounds prepared. In alcoholic solution it reacts with silver nitrate, to precipitate the silver salt, liberating nitric acid. The lead salt is soluble in ether owing to the doubly unsaturated fatty side chain, the lead salt of the hydrogenated acid is quite insoluble (cf. linoleic and stearic acids). Unlike the fatty acids anacardic acid resists the common methods of esterification. On heating ammonium tetrahydroanacardate to 200° in an attempt to prepare the amide, tetrahydroanacardol is formed.

173. Glutamic acid from cashew nut globulin.

M. DAMODARAN and T. G. SIVASWAMY, Madras.

A new globulin has been isolated from cashew nut (*Anacardium occidentale*) and analyzed by the method of Nitrogen Distribution described by one of the authors (M. D.). The high dicarboxylic acid content prompted the attempt to prepare glutamic acid from the protein, especially in view of the difficulty experienced in obtaining wheat gluten of good quality locally, which is necessary for the usual method of preparation. It has been possible to isolate from the new protein glutamic acid as the hydrochloride in yields comparable with those from gliadin.

174. Attempts towards synthesis of cantharidin.

H. H. IYER and P. C. GUHA, Bangalore.

The disodium derivative of ethyl-3 : 4-diketofuran-2 : 5-dicarboxylate (Johnson and Johns, *Amer. Chem. J.*, 1906, 36, 290) when reacted with ethylene bromide gave a substance melting at 175°. This is expected to be ethyl 2 : 3-diketo-1 : 4-endo-oxo-cyclohexane-1 : 4-dicarboxylate and has been successfully hydrolyzed to the corresponding diacid, m.p. 320° (decomp.) which has till now resisted all attempts to decarboxylation.

Similar reactions have been studied with trimethylene bromide and also using ethyl thiodiglycollate instead of ethyl diglycollate.

175. The precipitation of cystine by phosphotungstic acid.

M. DAMODARAN and T. G. SIVASWAMY, Madras.

The precipitation of cystine by phosphotungstic acid is known to be not quantitative, but in the Van Slyke method of analysis of proteins the cystine value still continues to be widely determined from the content in sulphur of the precipitate obtained when protein hydrolysates are treated with phosphotungstic acid. Serious error is assumed to arise only if the cystine has been subjected to prolonged boiling, and no systematic investigation appears to have been made on the influence of the concentration of cystine on the completeness of the precipitation. In the present study solutions of pure cystine in varying concentrations were subjected to treatment with phosphotungstic acid under conditions identical with those in the Van Slyke method, and the percentage of cystine precipitated at 20° and 30° respectively has been determined. The results show that at 30° proteins containing less than 3% cystine



would not produce any precipitate, while in those containing from 5 to 15% cystine, partial precipitation would occur ranging from 50 to 85% of the total cystine present. Similar results were obtained at 20°, except that a rather higher percentage of precipitation occurred. Thus in the most important types of proteins, where the cystine content is below 5%, cystine values obtained by precipitation with phosphotungstic acid are of no significance.

176. The stability of some substituted semicarbazides and thiosemicarbazides.

T. N. GHOSH, Bangalore.

When nitrophenylsemicarbazide is heated with excess of aniline at 140–150°, carbanilide in good yield is obtained. Similarly, thiocarbanilide is formed from nitrophenylthiosemicarbazide. These reactions can only be explained on the basis that the above semi- and thiosemicarbazides suffer fission at 140–150°, liberating cyanic and thiocyanic acids respectively which then react with aniline to form carbanilide and thiocarbanilide. This mechanism of the reactions further suggests that the additive reaction between nitrophenylhydrazine and HNCO or HNCS is reversible, though both the changes cannot be realized under the same conditions. Taking into consideration the general principle of correlation of additive process with tautomerism (Usherwood, *Chem. Ind.*, 1923, 42, 1246), the reversibility of the above additive process is of interest.

The above semi- and thiosemi-carbazides, when heated with normal alkali, suffer fission and yield benzo-azimidol, whereas *o*-nitrophenylthiocarbamide, under similar conditions, yields a benzotriazine derivative (Arndt and Rosenau, *Ber.*, 1917, 50, 1248).

177. Structure of chloroform, fluoroform, bromoform, and iodoform—their analogies with other chloroforms, viz. those of Ge, Sn, etc.

P. B. SARKAR, Calcutta.

Mechanism of several organic reactions where chloroform and alkali take part, e.g. preparation of salicylaldehyde, carbilamine, etc.

178. Nessler's reagents in the estimation of glucose.

M. GOSWAMI, H. DAS GUPTA, and K. RAY, Calcutta.

Further experiments have been carried on the estimation of glucose in various concentrations. Even a concentration of 0.02% gave very good result. Pathological urine also gave accurate results.

179. The synthesis of ring glycerides.

M. GOSWAMI and A. SHAHA, Calcutta.

Ring glycerides of the acids maleic, citraconic, phthalic, succinic have been prepared for the first time by using POCl<sub>3</sub> as condensing agent.

180. The preparation of organo-mercuric compounds by diazotization.

M. GOSWAMI, B. C. RAY, H. N. DAS GUPTA, and K. MUKERJEE, Calcutta.

This new method for the preparation of organo-mercuric compounds consists in diazotizing amino compounds and adding the diazo solution



to a solution of mercuric chloride when the organo-mercuric compound is precipitated.

181. Experiments on the catalytic oxidation of paraffin.

M. GOSWAMI, B. C. RAY, and P. DATTA, Calcutta.

It has been already shown that paraffin of m.p.  $50^{\circ}$  can be oxidized to a higher aldehyde when passed over nickel with oxygen (*J. Indian Chem. Soc.*, 1931, 8, 533). Experiments are now tried with lower aliphatic hydrocarbon like  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ; formaldehyde is found at about  $425^{\circ}$ . The reaction is facilitated by diluting the hydrocarbon with carbon dioxide.

182. Catalytic oxidation and dehydration.

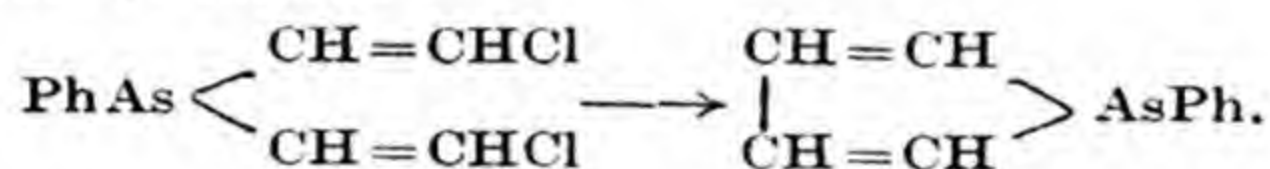
B. C. RAY, Calcutta.

By passing aniline with alcohol over thoria in the presence of oxygen, acetanilide has been obtained due to simultaneous oxidation and dehydration. Experiments are being carried out with other amines.

183. The synthesis of the arsenic analogue of pyrrole.

H. N. DAS GUPTA, Calcutta.

Attempts have been made with success to synthesize the arsenic analogue of pyrrole as follows :

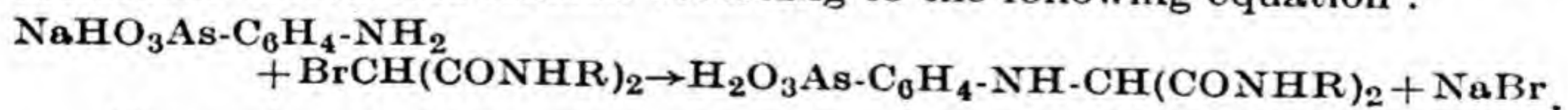


The structure of the above compound has been established by reducing the same to phenyl cyclotetramethylene arsine and determining the mixed melting point of the methiodide derivative and that prepared from 1:4-dibromobutane. Work on the synthesis of arsenic analogues of pyridine and succinimide is in progress.

184. A study of the interaction of atoxyl (sodium *p*-aminophenylarsonic acid) with the halogen derivatives of the substituted malonamides.

R. K. TRIVEDI and C. M. MEHTA, Baroda.

The chlorine atoms substituting the hydrogens of the reactive methylene group  $-\text{CH}_2-$  of substituted malonamides did not react with atoxyl, the bromo derivatives reacted according to the following equation :



The action of the following compounds has been tried : mono-bromo-malon-di-*p*-bromanilide, mono-bromo-malon-di-*p*-tolylamide, mono-bromo-malon-di-benzylamide.

The higher activity of bromine may be attributed to the higher atomic volume of bromine.

185. Loss of spirit due to evaporation under Indian conditions.

K. R. GANGULI, Agra.

Experiments were performed with spirits of different strengths ranging from 9.3 to 139.9% proof to study the percentage loss in proof gallonage and the proof strength of the alcohol by keeping them in bottles



of the standard quart size prescribed by the United Provinces Excise Department, uncorked but plugged with cotton wool in a way to admit air but to prevent dust to enter. The loss in proof gallonage and proof strength over a period extending about 12 months has been shown. The results represent practically the loss which may be expected in country spirits kept in bottles in more or less open condition in the dry atmosphere.

### BIO-CHEMISTRY.

186. The multiplicity of vitamin B<sub>2</sub>.

H. G. BISWAS and B. C. GUHA, Calcutta.

From parallel experiments on the flavine content and the vitamin B<sub>2</sub>-potency of different pulses and also of milk, it has been found that vitamin B<sub>2</sub>, as determined biologically, is a complex, of which the flavine (lactoflavine) is an essential component. The existence of other factor or factors (heat-stable) in this complex is indicated.

187. The relation between the composition of the diet and the urinary excretion of ascorbic acid.

A. R. GHOSH and B. C. GUHA, Calcutta.

In an investigation carried out in order to throw light on the metabolism of ascorbic acid in relation to dietary metabolism, it has been found that high-fat and high-protein diets lead to an increased excretion of ascorbic acid by the rat.

188. The stability of vitamin C in some food materials.

A. R. GHOSH and B. C. GUHA, Calcutta.

The estimation of ascorbic acid in some food-materials, after regular intervals of storage at 0°, shows that in some products the vitamin is particularly unstable, whereas in some it is fairly stable. In *bel* there is, if anything, a slight rise in the apparent ascorbic acid value after 15 days' storage at 0°.

189. Vitamin A assay of ghee.

B. N. BANERJEE and S. D. SUNAWALA, Bangalore.

The vitamin A content of Indian ghee has been estimated by the Carr and Price method following the 1932 B.P. The ultraviolet absorption at 328 mμ has also been measured with a Hilger H. 377 Vitameter. This can be done directly on ghee, as also via the unsaponifiable matter. Ghee is remarkably free from the interfering agents present in cod liver oils, so that such experiments are easy to perform. Even ten per cent. adulteration of ghee with oil, etc. can be easily and quickly detected in this way.

190. The formation of a reducing substance from mannose by means of tissues *in vitro* and *in vivo*.

B. C. GUHA and A. R. GHOSH, Calcutta.

Investigations have been carried out with the different tissues of the rat, rabbit, pigeon, guinea-pig, ox, fish, and snail regarding their capacity to convert sugar *in vitro* into a reducing substance (ascorbic acid ?) reacting with 2 : 6-dichlorophenol-indophenol. *In vivo* experi-



ment on rats and guinea-pigs have also been carried out. The urinary excretion of ascorbic acid (?) by rats after injection with mannose has been found to increase.

191. Colorimetric studies in enzyme action. Part I.

H. B. SREERANGACHAR and M. SREENTIVASAYA, Bangalore.

The qualitative detection and quantitative study of the course of enzyme hydrolysis can be followed colorimetrically when either the substrate or the products of reaction lend themselves to a colorimetric estimation. In the case of starch, the well-known blue colour, developed by the addition of iodine, can be made use of in following the enzymatic hydrolysis of starch, during which the colour progressively diminishes. A Lovibond Tintometer was used for the purpose of this study. Phosphatases on the other hand liberate the phosphorus from their respective substrates in an inorganic form and in progressively increasing quantities, so that the constituents can be estimated colorimetrically.

192. The action of the ultraviolet light on enzymatic reactions.

SOBHANLAL BANNERJEE and H. K. SEN, Calcutta.

In this work the protective action of nitrogenous compounds against the destruction of enzymes by the ultraviolet light has been described. Whilst diastatic activity is completely destroyed in the presence of the ultraviolet light, the addition of phenylaminoacetic acid, gelatine, ammonium citrate, etc., considerably reduce the destructive action. Analogously, if the substrate itself is a nitrogenous body, as for example, caseinogen, the hydrolytic action of pepsin or trypsin is not at all impaired by the action of the ultraviolet light. Pincussen's observations have not been generally confirmed, and the statement by him that the addition of a small amount of fresh enzyme revives the activity, could not be reproduced in the case of caseinogen investigated by the authors. The optimum pH for the pepsin action on caseinogen has been re-determined and found to be between 2 and 2.2. Analytical methods followed in the present work and in that of Pincussen have been discussed.

193. Method for detecting minute traces of urease and tyrosinase.

K. VENKATA GIRI, Bangalore.

Any substance containing urease sprinkled on the surface of a thin layer of agar gel containing 1% urea causes formation of  $(\text{NH}_4)_2\text{CO}_3$ . This diffusing through the gel produces a purple coloured zone on the addition of a drop of phenolphthalein on the surface. In a like manner, tyrosinase can be detected, by the production of a dark colour, when the enzyme material is added on to the surface of a tyrosine containing gel. The time allowed for diffusion is 24 hours.

194. The phosphatase activity of seeds during germination and its synthetic action.

K. VENKATA GIRI, Bangalore.

The phosphatase activity of a number of seeds during steeping and germination has been investigated. Repeated observations have shown that the activity increases four times that of the resting seed in the case of cholam (*Sorghum vulgare*), and about 30 times in the case of ragi (*Eleusine coracana*). This phenomenal increase in activity during germination has been further investigated with a view to throwing light on the mech-



anism. The probable rôle of activators and inhibitors during germination is being studied. The synthetic action of the enzyme during germination is also investigated.

#### 195. On salivary phosphatase.

K. VENKATA GIRI, Bangalore.

A phosphatase is present in human saliva which hydrolyzes  $\beta$ -sodium glycerophosphate into inorganic phosphorus. The optimum of activity of the phosphatase lies at 4.5 pH. In this respect it differs from other tissue phosphatases. It is suggested that acid phosphatase is typical of body fluids, and the alkaline phosphatase of the organs. The nature and the behaviour of the phosphatase with respect to the action of magnesium and other salts, the purification of the enzyme and the action of inhibitors are being studied.

#### 196. On liver amylase.

K. VENKATA GIRI, Bangalore.

Glycerol extract of acetone dried rat liver powder contains an amylase with a low maltose forming level, whereas the aqueous extract of the powder contains an amylase which has a high maltose forming function at the blue-violet iodine colour stage. Thus a complex system containing more than one amylase with varying degrees of maltose formation is present in liver. Further work is in progress to show whether the low maltose forming function of the enzyme present in glycerol extract is due to the presence of a specific inhibitor for the maltose forming enzyme, or whether it is a function of the enzyme molecule itself.

It has been further observed that of all the livers examined (sheep, swine, and rat), the liver of the rat contained a very active amylase.

#### 197. Corrosion of aluminium utensils.

S. V. GOVINDARAJAN and N. C. DATTA, Bangalore.

The present investigation has been undertaken with a view to studying the nature and extent of corrosion of aluminium utensils with acid food-stuffs containing salt, and also to working out methods for their protection.

Aluminium undergoes two types of corrosion, (1) general or uniform corrosion, and (2) formation of pits and blisters as a result of local action. The result of the present enquiry shows that with acid foods uniform corrosion is the general rule, whereas pits develop when foodstuffs containing salts are stored for fairly long periods. The rate of corrosion and also the tendency of pit formation depends on the quantities of impurities like iron and silicon present in aluminium vessels. The quantities of iron in different brands of aluminium vessels were found to vary from 0.39 to 1 per cent. 100 c.c. of 2% salt solution dissolved 3 times more aluminium from a vessel containing 1.02 per cent. of iron as compared with one containing 0.39 per cent. The quantities of aluminium dissolved do not increase proportionately with the increased concentration of salt. 100 c.c. of 1, 2, and 4% of salt solutions dissolved 1.1, 1.5, and 1.8 mgs. of aluminium respectively when stored for 72 hours. A thin coating of oil protects the vessels from the action of salt to a great extent but has only a slight effect in protecting against the action of acid and salt together. A film of oil applied before storing foodstuffs and also after cleansing the vessels, protects to a marked extent against pitting which generally develops on exposure. Results of repeated boiling and storage of foodstuffs with regard to corrosion and pitting are also discussed.



198. Absorption and excretion of tin by rats from food prepared and stored in tinned brass vessels.

N. C. DATTA, Bangalore.

Reviewing the literature on tin, Back (Food manufacture, 1933, 8, 381) writes that though tin is mostly excreted, there are indications that taken daily over for a long period, tin may be absorbed to produce minor disturbances in health or aggravate a condition of ill-health, and the subject needs reinvestigation from this aspect. Tinned brass vessels are extensively used in South India for the preparation and storage of acid foods containing salt with the result that varying quantities of corresponding tin salts are being constantly ingested along with the food. Investigation was therefore undertaken to study the rate of absorption and excretion of tin from food prepared in tinned vessels.

The results of metabolic experiments carried out on rats for a period of six months show that tin is mostly excreted in the faeces. The amount excreted in the urine varies from 4 to 6%. The quantity in the urine does not increase even after prolonged feeding, showing that the quantity of tin in circulation is very small. No serious poisonous symptom was observed in any case except that the body weights of tin-fed rats were about 20-25% lower than control animals maintained on food prepared in glass vessels.

Further investigation as regards the quantity of tin in various organs are in progress.

199. The effect of metal compounds on tissue phosphatase.  
I. The influence of lead salt.

K. VENKATA GIRI and N. C. DATTA, Bangalore.

Investigations have been undertaken to study the effect of lead salt on the phosphatase activity of different tissues. The results so far obtained indicate that kidney phosphatase purified by the method of Albers (*Z. physiol. Chem.*, 1935, 232, 189) is inhibited by lead salts in concentrations at which lead is considered to be toxic. The study is extended to the phosphatase of blood, bone, liver, and intestines. With a view to correlating the behaviour of lead salt *in vitro* and *in vivo*, experiments are being conducted with rabbits by injecting lead salts and determining the phosphatase changes in various tissues of the animals.

200. Determination of aluminium in biological materials.

S. V. GOVINDARAJAN, Bangalore.

A modified procedure based on the use of 8-hydroxyquinoline as the precipitant has been developed. Organic matter is destroyed by ignition at a low red heat (this is preferable to the slower and more cumbersome methods of wet digestion). Aluminium in the residue is extracted by hot alkali and freed from silica by addition of small quantities (about 0.2 g.) of a ferric salt. The alkali suspension is then raised to boiling point and filtered after cooling. The precipitate is washed repeatedly with cold, dilute alkali containing ferric hydroxide in suspension. The filtrate containing aluminium is then treated in the usual way.

The method has been successfully applied to the estimation of aluminium in water, sewage, soil, and biological materials in general.

201. Tubercles on water pipes.

S. CHELLAPPAN PILLAI, Bangalore.

Conflicting views are held with regard to the mode of origin, development, and persistence of tubercular structures on the inner sides of cast iron water pipes. While some hold that the mode of formation is purely



chemical, others adduce facts to show that the iron organisms like *Leptothrix*, *Crenothrix*, *Cladothrix*, *Gallionella*, and *Spirophyllum* are responsible for the phenomena. Again, opinion has been divided as to the source of the necessary iron for the incrustation, whether it is from the pipe itself or from the surrounding water through the agency of iron organisms. Further, how these incrustations gradually become compact and limpet-like structures, and how they manage to persist in spite of a regular current of water have not been adequately explained.

In the course of our studies on the subject the following observations have been made. (1) The tubercles are heterogeneous masses composed mainly of iron, to the extent of about 75 per cent. (2) This iron comes largely from the pipe itself. The water passing through the pipe contributes to the other mineral constituents, chiefly aluminium and silicon. (3) A lower form of fluorescent bacillus belonging to the *pseudomonas* genus has been invariably found associated with tubercles. The identity of this organism and its rôle in the formation of tubercle are under study.

## 202. A new bacterium from rotten potatoes.

H. K. SEN and G. C. DAS GUPTA, Calcutta.

A new type of facultative anærobic organism has been isolated from rotten potatoes. The optimum temperature and pH for the reaction are 42–45°, and 8–8.5 respectively. It can ferment starch and all pentose and hexose sugars. The products obtained by fermentation can be grouped under two heads: (i) Liquid products consisting of alcohol, formic and lactic acids and traces of acetone. (ii) Gaseous products consisting mainly of CO<sub>2</sub> and H<sub>2</sub>, with 3.4% of CH<sub>4</sub> only. The organism belongs to the same genus as the bacilli *actioethylicum* and *Macerans*, but is definitely of a different species. The main differences in its cultural characteristics from the other two, are the following: (a) It is non-motile, whereas the other two are motile. (b) It ferments galactose and lævulose both under aerobic and anærobic conditions, with either peptone or ammonium salts as the source of nitrogen. But *bacillus actioethylicum* ferments these two sugars under anærobic condition only, with ammonium salts as the source of nitrogen. *Bacillus Macerans* cannot at all ferment galactose and lævulose. (c) The most characteristic phenomenon in this case is that about 70% of the sugars are converted into lactic acid with a small quantity of succinic acid. No non-volatile acid is produced in the other two cases. Instead of acetic acid, formic acid is the only volatile organic acid produced, whilst alcohol as high as 25% of the quantity of sugar taken for fermentation has been recorded. These organisms have vegetative cells (2–4 $\mu$  × 1 $\mu$ ) having spores (2 $\mu$  × 1 $\mu$ ).

## 203. The fixation of atmospheric nitrogen in the soil and the utilization of molasses.

N. R. DHAR and S. K. MUKHERJI, Allahabad.

When sterile cane sugar solution and sterilized soil are exposed to sunlight in quartz vessels under sterilized conditions, the ammoniacal and total nitrogen are increased.

When air freed from bacteria and oxides of nitrogen and ammonia is passed through a solution of glucose or cane sugar mixed with freshly precipitated ferrous hydroxide, appreciable amounts of ammonia are formed.

It appears, therefore, that nitrogen fixation can take place in the complete absence of bacteria provided energy is available from the photochemical or induced oxidation of sugars.

When molasses are mixed with unsterilized soil and exposed to sunlight, the ammonia content goes on increasing with the exposure up to a limiting value.



Molasses when added to soil in the field also increase the ammoniacal and total nitrogen contents of the soil.

Molasses have been used as manure in increasing the yield of sugarcane to the extent of 36%. Rice cultivation is also improved by the addition of molasses to the soil.

204. Some aspects of the mechanism of the fixation of atmospheric nitrogen in nature.

T. R. BHASKARAN, Bangalore.

It has been suggested by a number of previous workers that carbohydrates are the chief starting material for non-symbiotic fixation of atmospheric nitrogen, though small quantities may be fixed in the presence of other organic substances as well.

In the course of our studies on the fixation of nitrogen with the mixed flora of the soil, it was observed that glucose which was provided as the organic nutrient was completely decomposed in the course of the first four days, being mostly converted into gases. Of the residual organic matter, about 35 per cent. was accounted for by organic acids (chiefly lactic, acetic, propionic, and butyric), the rest being mostly present as micro-organisms (living as well as dead). During that period only about a third of the usual quantity of nitrogen was fixed and, of this, the major part was present in a water soluble form. In the subsequent period a large part of the organic acids was lost, with a corresponding increase in mucilage. There was also rapid fixation of nitrogen. After the twelfth day there was slight loss of organic carbon, but there was no appreciable fixation of nitrogen.

The results show that in nature (a) the carbohydrate is not directly utilized for fixation, (b) that the organic acids formed by the decomposition of the carbohydrate contribute largely to the growth of organisms and nitrogen fixation, and (c) that the production of mucilage and nitrogen fixation, though related, are not directly proportional to each other. The studies are now being extended to pure strains of nitrogen fixers present in the soil.

205. The mechanism of nitrogen fixation by azotobacter.

M. SREENIVASAYA, Bangalore.

A critical review of the theories relating to the mechanism of nitrogen fixation is presented. The rôle of the mucilage or the slime that characteristically precedes the fixation is discussed. It is suggested that the efficiency of a given type of carbohydrate for nitrogen fixation is related to its percentage of convertability into mucilage.

If one invokes the aid of the highly efficient slime-formers capable of attacking the resistant types of carbohydrates like cellulose, a favourable medium for the nitrogen fixers can be created in an environment not ordinarily suitable for the direct and independent action of azotobacters. This circumstance suggests the possibility of employing a mixture of the organisms symbiotically for the fixation of nitrogen where resistant types of celluloses are utilized as the source of energy.

206. On the mechanism of biological oxidation of ammonia by the nitrite forming bacteria.

G. GOPALA RAO and K. M. PANDALI, Waltair.

From experiments on the oxidation of ammonia by pure cultures of the nitrite-forming bacteria it is concluded that hydroxylamine and hyponitrous acid do not form the intermediate products in the oxidation of ammonia to nitrite. These compounds could not be detected in several



hundreds of cultures examined by various delicate tests. The positive results obtained by Mumford, Beeseley, Corbet, and Maze may be due to the impurity of the cultures and Kluyver and Donker's support to these is not based on experiments, but on mere speculation. Recently Nelson has obtained results similar to ours by pure culture studies.

The influence of various capillary active substances and specific poisons like the cyanides, urethanes, hydrogen sulphide, complex cyanides, etc. has been studied by the Erlenmeyer flask technique. From these experiments it is concluded that the oxidation is a surface catalytic reaction occurring on the surface of the bacteria at certain active centres containing iron.

## 207. Denitrification in sunlight and its retardation.

N. R. DHAR and S. K. MUKHERJI, Allahabad.

The velocity of the thermal and photochemical decomposition of an aqueous solution of  $\text{NH}_4\text{NO}_2$  has been determined at  $40^\circ$  and  $50^\circ$ . The velocity of the thermal decomposition is increased by an increase of temperature, but the photochemical velocity is slightly affected by an increase of temperature. The ratio of photochemical to the thermal decomposition of  $\text{NH}_4\text{NO}_2$  is higher at  $40^\circ$  than at  $50^\circ$ ; i.e. when the temperature is high, the thermal decomposition of  $\text{NH}_4\text{NO}_2$  is marked.

Copious decomposition of mixtures of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{KNO}_2$  in the presence of dry soil and exposed to sunlight in the months of April, May, and June has been observed.

A solution of  $\alpha$ -alanine and  $\text{KNO}_2$  mixed with soil and exposed to sunlight undergoes considerable loss of nitrogen.

Sterile solutions of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{KNO}_2$  mixed with sterilized soil when exposed to sunlight in quartz boiling tubes show considerable decomposition with evolution of gaseous nitrogen.

Organic manures, e.g. oil cakes, green manure, farmyard manure, molasses, etc. produce beneficial results, especially in tropical countries, not only by increasing the colloidal content and water retention power of the soil, but also by protecting the soil nitrogen by decreasing the velocity of the formation and decomposition of ammonium nitrite.

## 208. The determination of nitrogen in yeast.

S. RAJAGOPAL, Bangalore.

It is well known that yeast is highly resistant to acid digestion. The process of digestion is very slow and often yields low and discordant estimates even after a colourless digest is obtained.

It has been found that pre-treatment with water or mild oxidizing agents greatly hastens the rate of digestion. Pre-treatment with 20 per cent. caustic alkali is even more effective. The cells are either disintegrated or rendered more penetrable so that the subsequent digestion proceeds rapidly to completion.

## 209. The milling quality of raw and parboiled rice.

A. SREENIVASAN and H. P. DAS GUPTA, Bangalore.

Although the chemical changes attendant on parboiling are essentially similar, irrespective of the time and temperature of soaking the paddy or the time of steaming and the pressure of the steam, yet the milling quality of the rice, as determined by the percentage of whole kernels yielded, varies widely with different treatments. Different varieties of paddy respond also very differently on parboiling in regard to milling quality. Parboiled rice always mills better than raw (untreated) rice. However, the rate of milling being the same, the percentage of polishings removed from parboiled rice is far less than with raw rice. The milling



quality of both raw and parboiled rice decreases with increase in the degree of milling. But, with a high degree of milling, parboiled rice appears to be poorer in milling quality than raw rice. The optimum conditions of parboiling, with a view to obtaining a rice of high milling quality, varies for different varieties.

Parboiled hulled rice is always darker in colour than raw rice, though on polishing the extent of coloration is much less. Cooked parboiled rice is nearly as white as raw rice. The colour of the parboiled rice would appear to depend on the time of soaking the paddy, the temperature of the steep water, the time and pressure of steaming, also probably on the colour of the husk. Work is in progress relating to the keeping and cooking quality of raw and parboiled rices, polished and unpolished.

## INDUSTRIAL CHEMISTRY.

### 210. A domestic smokeless oven.

H. K. SEN, R. M. PAL, and KANAILAL ROY, Calcutta.

A preliminary report of this was published some time ago in the *Proc. Inst. Chemists (India)*. Since then, the question of the storage of the gas produced in the coking of coals used in domestic fire places has been studied, and three types of holders for the gas appear to recommend themselves according to the magnitude of domestic requirement. (i) If the consumption of coal is very moderate, say 10–15 lbs. a day, then the installation of a small gas holder working on the principle of an aspirator, is undoubtedly the most convenient. The holder is made broad and squatty, having an upper chamber to enable it to be filled with water from time to time. The cooking of the evening can be almost entirely effected by this collected gas of the midday cooking. (ii) The second type of gas holder is a divided cylinder or drum of appropriate diameter, the dividing shelf being perforated. This cylinder or drum can be rotated on an axis. The gas from the coking oven enters the top chamber, whilst the water descends through the perforated shelf, and expels any gas that had collected at a previous stage. When the evolved gas nearly expels the total quantity of water from the upper compartment (as can be seen from a levelgauge), the operator has simply to rotate the drum by hand through 180°, and the collection of gas continues. In this case the generation and the use of gas are simultaneous. (iii) The direct burning of the gas by a specially adjustable burner is also possible, although storing is more convenient, whether for heating or for small power purposes. For every pound of coal, two cubic feet of gas, about an ounce of tar, and approximately 11.5 ounces of coke are produced. If the city of Calcutta consumes 4 million tons of coal as domestic fuel, then by creating a collecting organization for the tar, about 50 million gallons of tar could be annually utilized for the fuel, or for the dye industry.

### 211. The possibility of aluminium production in Bombay.

M. S. PATEL, Bombay.

The discovery of bauxite deposits near Bombay by the author, as anticipated by Dr. C. S. Fox, opens up a new field for the utilization of surplus hydro-electric power at Bombay. The deposit on the Tungar hill near Bombay has been prospected, and nearly 300 samples of bauxite from the deposit have been analyzed. The average composition runs as follows :—

Alumina, 54 to 59% ; Silica, 0.3 to 0.8% ; Iron oxide, 3 to 11% ;  
Titanium oxide, 2 to 6% ; Compound water, 28 to 31%.



The estimated quantity of bauxite on the plateau works out at one million tons. Alumina has been prepared from an average sample of the bauxite, by the Bayer process on a laboratory scale, with the following composition :—

Alumina, 99.34%, Ignition 0.28%, Soda 0.25%.

Another important raw material for the production of aluminium is petroleum coke for the production of electrodes. Samples of petroleum coke from oil distilleries operating in India have been obtained and examined. The coke produced by the refineries of the Burmah Oil Co. Ltd., which analyzes as : Moisture 0.01%, Volatile matter 9.79%, Sulphur (included in volatile matter) 0.47%, Fixed carbon 90.18%, Ash 0.02%,—has been found to be most suitable for aluminium production.

Probable sites with unlimited water supply and adequate water transport facilities have been surveyed, and waters have been tested as to their suitability for the generation of steam, and for process work in the production of alumina.

The cost of raw materials at possible sites have been worked out per ton of aluminium produced. These compare very favourably with those prevailing at centres of aluminium production abroad. The estimated total cost of production of aluminium ingots works out at Rs. 985 per long ton for a plant producing 3,000 tons of aluminium per annum; this figure includes the depreciation on the machinery, equipment and buildings, and the cost of labour, supervision, technical control and management. The cost of power is calculated at 2½ pies per K.W.H. delivered at the works.

## 212. An investigation on the curing of hides with different mixtures of sodium sulphate and chloride in comparison with khari salt.

B. M. DAS, B. B. DHAVALÉ, and B. N. PAL, Calcutta.

It is a common practice in Bengal to cure hides with khari salt, a saline earth containing various proportions of sodium sulphate and chloride as its two principal preservatives. The curers taking advantage of the presence of the earthy matter often intentionally load the hides with mud and sand and thus the plaster-cured hides of Bengal have been brought into bad repute. With a view to finding out a cleaner and equally effective substitute for khari salt the present investigation was undertaken with different mixtures of anhydrous sodium sulphate and chloride.

The hides treated with different cures were preserved for eighty weeks and observations were made from time to time. It was observed that (1) sodium sulphate or sodium chloride when used alone could not preserve the hides for more than six weeks; (2) the mixtures in which sodium sulphate predominates preserve the hides better than those in which the amount of sodium chloride is greater; (3) the mixture containing 5 parts of anhydrous sodium sulphate : 1 part sodium chloride preserves the hide best and for the longest period; the khari salt sample containing the said proportion of these constituents also yielded a similar result.

## 213. The extraction of nicotine from Bombay tobaccos and tobacco waste.

V. C. AMIN and M. S. PATEL, Bombay.

Nicotine has been extracted by various methods from samples of tobacco grown in various districts of the Bombay Presidency and from tobacco waste. The steam distillation method has been found to be most practical for Indian conditions. A sample of nicotine sulphate



of standard concentration has been prepared and tested entomologically, with the result that the product prepared in our laboratory showed almost the same insecticidal value at higher concentrations as the imported material, and about 10% less at lower concentrations.

Nicotine borate and nicotine arsenate have been prepared and analyzed. Both these are solids and very soluble in water. The borate decomposes and chars on heating without melting, while the arsenate melts at 150°. The insecticidal values of these two compounds are being studied, and are likely to prove very useful solid nicotine insecticides.

The nitrogen content of the tobacco before and after the extraction of nicotine has been determined. The ash of nicotine extracted tobacco has been analyzed with a view to its possible utilization.

#### 214. The continuous hydrogenation of oils.

S. K. KULKARNI JATKAR and V. T. ATHAVALE, Bangalore.

Continuing the previous work in our laboratory (J. G. Kane, *Proc. Sci. Congress*, 1935, Calcutta), we are studying the comparative activity of different preparations of nickel catalysts in a continuous process under different pressures. We have found that the wire form of catalyst is most readily prepared in a high state of activity for routine laboratory work.

A plant producing one ton of hydrogenated oil per day is also being fitted up for studying the working of the highly active silica gel catalyst discovered in our laboratory.

#### 215. Base exchange by permutit in molasses.

S. D. AGNIHOTRI and S. K. K. JATKAR, Bangalore.

Although the commercial possibilities of the use permutit in sugar refining are well known, the method of its use in refining cane molasses has not so far been studied in detail. The method of replacing the potassium ions which impart a bitter taste to molasses, by ammonium ions, and the subsequent removal of ammonia by concentration, has been studied by using the conductivity method and checking the results by direct analysis. The product so obtained was inferior to that obtained by removing the salt by electrodialysis. The influence of pH of molasses on the base exchange is being studied.

#### 216. The removal of salts from cane molasses.

S. D. AGNIHOTRI, Bangalore.

Molasses, diluted to different concentrations and clarified by centrifuging, were electrodialyzed for a period of 8 hours, using carbon electrodes and silk and ordinary filter cloth with chrome gelatine coating as the most effective anodic and cathodic membranes. The resulting solution after neutralizing with calcium carbonate was concentrated under vacuum, and the product, though still dark in colour, is found to have no undesirable smell or taste.

#### 217. Plastics from corrosive oils.

S. D. AGNIHOTRI and S. K. K. JATKAR, Bangalore.

Experiments have been conducted to make bakelite-like products from cashew shell oil and marking nut oil by condensing these with hexamethylenetetramine, tannins, sugars, and molasses. The products with the latter three were always hygroscopic, and with hexa were very brittle and unsuitable for moulding. Although marking nut oil is the more suitable of the two, it is concluded from numerous experiments



that these oils are not suitable for making plastics. The observations are in harmony with the chemical investigations about the nature of the main constituent of these oils as found by Pillay and co-workers (*J. Indian Chem. Soc.*, 1931, 8, 517; 1935, 12, 226, 231).

218. A new process for the solvent extraction of castor seed with rectified spirit.

N. G. CHATTERJEE, Cawnpore.

The process is an adaptation of the battery extraction system to suit the requirements of the peculiar properties of castor oil and rectified spirit based on laboratory experiments. The special feature of the process is the method by which the solvent is removed from the extracted oil, and its recovery for reapplication in the process, involving an expenditure of steam which is considerably less than is usually the case in solvent extraction processes. It has been found that by this process 63.5% of oil was obtained out of a total oil content of 64.6% in a sample of decorticated seed, while the maximum loss in solvent would be within 1%.

219. A new method of recovering sugar from *gur* without the production of molasses.

N. G. CHATTERJEE, Cawnpore.

It is well known that one of the main causes of the production of molasses is the use of lime during the process of the preliminary treatment of *gur* solution. In the present method, the albuminous matter, phosphates, and other impurities are removed without the use of lime or any other alkaline hydroxides, while the separation of the sucrose from invertose is carried out by fractional crystallization and precipitation. The process can easily be adopted commercially and may be economically worked on even a small scale.

220. The recovery of potash from ashes.

V. C. AMIN and M. S. PATEL, Bombay.

Ashes have been an important source of potash from time immemorial. Even in the present century small scale potash extracting plants came into existence both in Europe and America during the war.

Potash salts have been extracted from two samples of ashes: from ordinary Bombay household ash and from tobacco stalks. A very simple process capable of being operated by an ordinary village worker of common intelligence has been worked out for the recovery of potassium salts and potash at ordinary temperature.

Bombay ash gives  $K_2CO_3$  and KOH with some soda compounds. The ashes from tobacco stalks give on the average 30% soluble salts, which give an actual yield of 59% KCl, 19%  $K_2CO_3$ , 2% KOH, 20%  $K_2SO_4$ . On further crystallization potassium chloride and potassium sulphate are recovered in almost pure state. It is not possible to effect complete separation of  $K_2CO_3$  and KOH. The mother liquor after the recovery of  $K_2SO_4$  and KCl contains  $K_2CO_3$  and KOH. Some carbonate separates out on slow evaporation at ordinary temperature, leaving a viscous liquid containing  $K_2CO_3$  and KOH. It is necessary to heat this residue in order to get a dry product. The economics of the process are being worked out.



## 221. Pastes for storage battery grids.

B. S. SRIKANTAN, Waltair.

The usual recipes given in books and patent literature for the making of pasted electrodes of storage batteries did not give good results. Usually the fillings, apparently good, crumbled to powder when immersed in the electrolyte.

After several trials a composition has been arrived at which is very hard and adherent, and which can be filled in the positive or the negative grid. The negative plate formed by reduction of this for 24 hours at a current density of 1.5 amp. is spongy and yet strongly adherent to the grid. The positive plate is formed in 12 hours at a current density of 1.0 amp., giving a hard buff-coloured peroxide of lead.

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## 222. Photo-voltaic cells containing dye solutions.

B. S. V. RAGHAVA RAO *and* D. S. NARAYANAMURTI, Waltair.

## 223. A new cell for electrolytic rectification.

D. S. NARAYANAMURTI, Waltair.

## 224. A simple method for estimating carbonates in soils.

S. DAS, Pusa.

## 225. The partial coagulation of colloids.

S. GHOSH, Allahabad.

## 226. The reduction of freshly prepared molybdic acid solution by glucose in dark and sunlight.

A. K. BHATTACHARYA *and* S. GHOSH, Allahabad.

## 227. The swelling of gels.

N. A. YAJNIK *and* ASA SINGH, Lahore.

## 228. Studies in colloidal behaviour of Indian gums.

N. A. YAJNIK *and* MANPHUL SINGH JAIN, Lahore.



**DISCUSSIONS.****I. THE SCOPE OF PREPARATION OF FINE CHEMICALS IN INDIA.**

S. S. BHATNAGAR, B. B. DEY, N. R. DHAR, J. C. GHOSH, P. C. GUHA, P. NEOGI, J. N. RAY, H. K. SEN, B. K. SINGH, T. S. WHEELER, and others are expected to speak.

**II. THE UTILIZATION OF MOLASSES.**

N. G. CHATTERJEE, N. R. DHAR, R. C. SRIVASTAVA, V. SUBRAMANYAN, and others are expected to speak.

**JOINT DISCUSSION.**

*Mathematics and Physics and Chemistry Sections.*

**THE STRUCTURE OF MOLECULES.**

P. C. GUHA, Bangalore, will preside.

P. N. GHOSH, Calcutta, K. S. KRISHNAN, Calcutta, R. SAMUEL, Aligarh; and J. C. GHOSH, Dacca, B. B. DEY, Madras, MATA PRASAD, Bombay, P. R. RAY, Calcutta, and others are expected to speak.











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# INDIAN SCIENCE CONGRESS

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*Twenty-fourth Annual Meeting*

HYDERABAD, 1937

## ABSTRACTS

### *Section of Chemistry*

*President:*—PROF. J. N. RAY, Ph.D., D.Sc., F.I.C., F.N.I.

CALCUTTA

ROYAL ASIATIC SOCIETY OF BENGAL, 1, PARK STREET







# SECTION OF CHEMISTRY

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## *Abstracts*

### Inorganic Chemistry

#### 1. Some compounds of boron, hydrogen and oxygen.

R. C. RAY, Patna.

When magnesium boride is treated with water, out of contact with air, a powerfully reducing solution is obtained. From this solution, two isomeric compounds of the formula,  $K_4H_2B_2O_2$  together with two other compounds having the formulæ,  $K_4H_2B_2O_2$  and  $K_2H_2B_2O_2$ , respectively, have been isolated. The constitution of these compounds has been discussed. The mechanism of their formation and their relationship with boron hydrides have been suggested.

#### 2. New compounds of gallium. Part II.

P. NEOGI and S. K. NANDI, Calcutta.

A hydrated oxide  $Ga_2O_3 \cdot H_2O$ , chlorate, bromate, iodate, metaphosphate, phosphate and basic phosphates of gallium have been prepared.

#### 3. Substituted cyano-cobaltates. Aquo-pentacyano-cobaltic acid and its salts.

P. RAY and N. R. DUTT, Calcutta.

In continuation of the investigation on the substituted cyano-cobaltates by one of us (P.R., *Zeit. anorg. u. allg. Chem.*, 1931, 199, 353; 1933, 211, 173; 1934, 220, 153), aquo-pentacyano-cobaltic acid and its salts have now been prepared and their properties studied. The parent aquo-compound was obtained by the oxidation of previously described thiosulphato-pentacyano-cobaltate with hydrogen peroxide in an almost neutral solution. Besides the free acid, alkali, alkaline-earth and some heavy metal salts have been described. The yellow silver salt, on dehydration, gives a blue penta-co-ordinated practically diamagnetic compound. This is rather unique. The free acid itself is, however, not very stable.

#### 4. Resolution of co-ordinated inorganic compounds. Part II.

P. NEOGI and K. L. MANDOL, Calcutta.

Twenty-four co-ordinated compounds of cadmium containing: (1) two molecules of ethylenediamine and one molecule of propylenediamine, and (2) one molecule of ethylenediamine and two molecules of propylenediamine have been prepared and the optical rotations of the active compounds have been measured.



## 5. Studies in the pseudo-alums.

P. B. SARKAR and B. C. RAY, Calcutta.

A systematic study of the complete poly-therms of various sulphates of magnesium group of metals with aluminium sulphate and water has been undertaken.

## 6. The action of hydrogen sulphide on sodium nitrite and lead nitrite.

H. B. DUNNICLIFF, SARDAR MOHAMAD, and MAHARAJ KISHEN, Lahore.

The reduction of sodium nitrite in solution yields sulphur and the polysulphides of ammonium and sodium but not hydroxylamine. Its reduction in the solid state produces an explosive yellow compound which appears to have the composition  $\text{NaNO}_2\text{H}_2\text{S}$ .

The reduction of lead nitrite gives nitrous oxide, nitric oxide, nitrogen hydroxylamine, sulphur, ammonium sulphate and lead as sulphide and sulphate. The reduction is apparently controlled by the catalytic action of nascent nitrous acid.

## 7. Polymerisation of sulphur monoxide.

B. SANJIVA RAO and M. R. ASWATHNARAYANA RAO, Bangalore.

Further work on sulphur monoxide in tetrachlorethylene solution (cf. B. S. Rao and M. R. A. Rao, *Current Sci.*, 1935, 6, 406) has given evidence of polymerisation of the monoxide to form thiosulphuric anhydride. The monoxide when adsorbed on silica gel yields the polymerised form as revealed by certain experiments.

## 8. Constitution of hypo-nitrous acid from physico-chemical studies.

P. B. SARKAR, B. C. RAY, and J. GUPTA, Calcutta.

## 9. Constitution of iodic acid.

M. R. NAYAR and L. N. SRIVASTAVA, Lucknow.

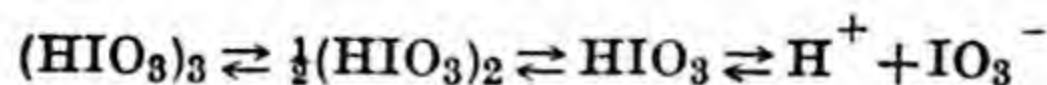
Aqueous solutions of the acid of 14 different dilutions varying from 0.01N were prepared and their physical properties investigated. The specific property of the solute is determined from the mixture law equation:

$$P_{\text{soln.}} = P_{\text{solvent}} (1-x) + P_{\text{solute}} (x)$$

where  $P$  denotes the property like density, viscosity, refractive index, etc., and  $(x)$  and  $(1-x)$  are the molecular fractions of the solute and solvent respectively.

When  $P_{\text{solute}}$  is plotted against the concentration, the graph is found to be not a straight line, nor even a continuous curve. In the case of viscosity, for example, there are three parts of the curve (2nd and 3rd convex towards concentration) intersecting at 0.04N and 0.1N. The minima correspond to 0.05—0.06N and 0.4N—1.0N.

Such a behaviour was expected from freezing point and other experiments (*Zeit. anorg. Chem.*, 1934, 220, 163) and may be explained by the reaction:





## 10. Studies in hydrates of zinc sulphate in presence of sulphuric acid.

N. K. JOSHI, Bombay.

*(Communicated by P. M. Barne, Bombay.)*

It is well known that the hydrates of a salt are stable only within a certain range of temperature and that in general as the temperature rises, progressively lower and lower hydrates are formed. It is difficult to work at high temperatures and examine the various hydrates formed.

It is reported (H. W. Foote, *J. Amer. Chem. Soc.*, 1915, 37, 290) that extremely soluble acids like hydrochloric, sulphuric, nitric or extremely soluble salts like magnesium chloride have a dehydrating effect. Therefore it may be possible to observe the formation of several hydrates—stable at different temperatures by the addition of varying amounts of an acid (or a neutral salt) to the solution at a fixed temperature. For zinc sulphate the only hydrates so far reported are the hepta, hexa and mono hydrates. The methods employed were the determination of (a) the solubilities at various temperatures, and (b) vapour pressure. It is possible that some of the hydrates might have escaped detection if their transition range was very small. But by progressive small additions of sulphuric acid we should be able to detect the formation of any intermediate hydrates. With this in view, all the possible hydrates of zinc sulphate at 30°C and 45°C were studied in presence of varying amounts of sulphuric acid. The method adopted was Schreinemakers's 'residue' method (*J. Amer. Chem. Soc.*, 1924, 46, 1766) for the determination of the solid phase in the solubility bottles designed by N. Campbell (*J. Chem. Soc.*, 1930, 179).

It has been found that the addition of sulphuric acid considerably diminishes the solubility of zinc sulphate, whilst the solid phase undergoes a variation identical with that produced by increase of temperature in pure aqueous solutions. As the concentration of the acid is increased, the hepta, hexa and mono-hydrates become the only stable solid phase in equilibrium. Investigation of hydrates of other salts by this method is in progress.

## 11. Hydrolysis of uranyl salts.

BALWANT SINGH, G. AHMAD, and H. B. DUNNICLIFF, Lahore.

The hydrolysis of uranyl nitrate, uranyl sulphate and uranyl acetate has been studied at 30°C by the electromotive force method, using the quinhydrone electrode. The order of salt hydrolysis has been found to be as uranyl nitrate > uranyl sulphate > uranyl acetate. The degree of hydrolysis increases with dilution. The results obtained compare well with the degree of hydrolysis determined by Bruner (*Zeit. physikal. Chem.*, 1900, 32, 133) at 40°C for the nitrate and the sulphate by the sugar inversion method.

## 12. An examination of a very insoluble phosphate extracted from monazite obtained from Orissa. Part II.

C. B. ROY and S. B. ROY, Sabour.

The present paper is a continuation of the work described in (1) *J.S.C.I.*, 1933, 745, and (2) *Zeit. anorg. Chem.*, 1933, 216, 203.

The refractory phosphate referred to in (2) has been further investigated. Attempts at further purification of the base led us to the clue that the chloride could be divided into two portions: (a) colourless crystals insoluble in conc. hydrochloric acid, and (b) a yellow portion soluble in conc. hydrochloric acid. After repeated treatment, the solution of the yellow portion was so far purified that by spectroscopic examination, kindly undertaken by Profs. K. Prasad and D. K. Bhattacharya, Science



College, Patna, there was no evidence of the presence of Zr, Hf or Ti. We do not think, however, that the presence of traces of Ce indicated by spectroscopic evidence, still tenaciously retained after our exhaustive treatment, can fully explain the peculiarities of the base mentioned in our paper (2).

Further examination of (a) and of (b) by spark spectra for which fresh quantity of monazite has to be broken up again and subjected to the laborious operation described, is in progress.

### 13. Influence of light on iodine vapour at 250°.

T. SURYANARAYANA, Waltair.

Iodine vapour enclosed in an evacuated soft glass bulb kept at a temperature of 250°–300°C is exposed to light from a 1,000 watt Tungsten filament lamp. After two days white solid substance is found deposited on the glass wall. On breaking the bulb the white substance became a brown liquid. The nature of the white substance is under investigation and it is supposed to be silicon iodide.

### 14. Decomposition of the sulphates of calcium, strontium and barium.

S. M. MEHTA and H. A. COOPER, Bombay.

The decomposition of the sulphates of calcium, strontium and barium in the presence of different amounts of boric anhydride has been studied at temperatures between 900° and 1100°C. It is found that these substances decompose to give mostly sulphur trioxide with a small proportion of sulphur dioxide. It has been possible to effect nearly ninety-two per cent decomposition of calcium sulphate at a temperature of about 1,000°C. The effect of the addition of iron, nickel and carbon on the decomposition of calcium sulphate has also been investigated and it is found that the temperature of decomposition is appreciably lowered by the addition of these substances. The decomposition of the alkaline earth sulphates under identical experimental conditions has been compared. It is suggested that the residue may be utilized to give (i) glass, (ii) acid, or (iii) borax.

### 15. Electro-deposition of chromium from potassium dichromate baths. Part III. In presence of borate.

M. A. ALI and S. HUSSAIN, Hyderabad-Deccan.

Electrolysis of baths containing potassium dichromate and a high concentration of boric acid with a low current density at 40°C yielded white tenacious deposits of chromium. The current efficiency was lower than in the case of baths containing potassium dichromate and sulphuric acid or acetic acid. When dichromate was substituted by chromate or boric acid by borate, no white deposit was obtained. Change of distance between the electrodes had considerable effect on the deposit. Lead anodes were as good as platinum anodes.

### 16. Electro-deposition of copper on glass surfaces.

S. S. JOSHI and S. S. KULKARNI, Benares.

It has been found that considerable difficulties exist in the preparation of copper films on glass, when produced by the reduction of suitable copper salts. These are chiefly in respect of the chemical purity, homogeneity and the optical regularity of the reflecting surface. Satisfactory results were, however, obtained when silver films produced by some of the well known chemical methods were used as a conducting base, for



subsequent electro-deposition from copper baths. The usual cupro-cyanide method (also that involving the use of copper sulphate) could not be employed, as this weakened the initial silver base. In certain ranges of temperature and concentrations for which data have been worked out, copper acetate and cuprammonium solutions (both when copper salts, copper hydroxide, or even when metallic copper in the presence of oxygen, were treated with strong ammonia) gave stable copper films with characteristic mirror properties, which have been studied.

17. Elementary and mixed metallic films by electrodeposition on glass surfaces.

S. S. JOSHI and N. HANUMANTHA RAO, Benares,

Detailed studies have been made of: (a) the conditions for silver deposition from solutions as dilute as 0.01 per cent silver nitrate, (b) the chemistry of the pre-treatment of the glass surface, (c) the kinetics, the spectral sequence of the play of colours during the production of the silver mirror, (d) the influence of temperature, (e) surface conductivity, (f) microscopic examination of the surface structure of the mirror, (g) the effect of extraneous materials in small amounts, e.g., potassium hydroxide, certain electrolytic coagulants, gelatin, etc. Data are given for the absorption limits of these silver films both when pure, and when superimposed with extremely thin deposits of gold and nickel produced electrolytically. Interesting results were obtained on the mobilization of the particles at low temperatures (about 300°C.) and the corresponding shift in the absorption limits.

18. A new method for the estimation of bromides.

M. R. VERMA, P. L. KAPUR, and M. ANWAR-UL-HAQ, Lahore.

The bromide solution is treated with a mixture of 10% chromic acid and 10% nitric acid and bromine so liberated is extracted repeatedly with carbon tetrachloride. The estimation is carried out by treating the extract with potassium iodide and titrating the liberated iodine against sodium thiosulphate.

19. Analysis of type metal.

P. R. SUBBARAMAN and K. R. KRISHNASWAMI.

Lead-tin-antimony alloys offer considerable difficulties in analysis. The methods so far suggested are either tedious or involve special apparatus.

Several alloys of lead, tin and antimony of known composition have been prepared and their analyses carried out by different procedures with a view to evolve a convenient and reliable method. The results obtained are described in the paper.

20. Electrometric titration of dibasic acids.

C. T. ABICHANDANI and S. K. K. JATKAR, Bangalore.

The differential titration curves for oxalic, malonic, succinic and adipic acids by sodium hydroxide solution (N/10) containing small quantities of carbonate revealed the pronounced negative values near the end point and minor inflexions at the half neutralization points, the values of the former being inversely proportional to the strength of the acid. The titration curve of adipic acid is not similar to that of succinic acid as reported by Chandler.



## 21. Tourmalines from the Mysore state.

K. Y. SREENIVASA, Iyengar.

Various specimens of tourmaline obtained from the Director of the Mysore Geological Department have been subjected to careful chemical analysis and the results obtained are mentioned and discussed in this paper.

An account is given of the difficulties met with in the determinations of boron, fluorine and water in tourmaline, and also of the precautions to be taken to obtain reliable results.

## 22. Reduction of iron content of native pyrolusite.

S. VENKATASUBBA RAO *and* K. R. KRISHNASWAMI.

The Indian deposits of pyrolusite are too high in iron to satisfy some specific commercial requirements. Samples from a deposit in Mysore State carrying 85 per cent.  $\text{MnO}_2$  and 3.5 to 4 per cent. of Fe were submitted to various method of treatment, e.g., Wilfley table, electro-magnetic separator and chemical reagents.

The results obtained are discussed in the paper.

## Physical Chemistry

## 23. Decomposition of nitric oxide under silent electric discharge.

S. S. JOSHI *and* K. C. SHRIVASTAVA, Benares.

A detailed study of this decomposition has been made (under a given group of electrical factors) of the influence of the addition of moisture,  $\text{N}_2$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{H}_2$  and  $\text{SO}_2$  in varying proportions. The decomposition of nitric oxide in the discharge is retarded to an extent which increases by increasing the proportion of the foreign gas. The 'electron affinity' of the latter has been found to be an important determinant of this power of retardation. The current through the reaction space varies discontinuously indicating intermediate changes; of these one has been established to be the formation and subsequent decomposition of nitrogen peroxide. Measurements have been made of the 'threshold potential' during the complete decomposition of the gas both when pure and in the presence of the above mentioned foreign gases.

## 24. The hydrogen-chlorine interaction under electric discharge.

S. S. JOSHI *and* P. N. BHARGAWA, Benares.

The principal data in the literature for the production of this reaction refer to the use of  $\alpha$ -rays, radiations of different frequencies and heat (dark reaction). We have studied this under the influence of electrical discharge due to alternating fields of low frequencies. Measurements were made of (a) the potential applied to the reaction vessel, (b) the current flowing through the latter during the reaction, and (c) influence of independently present excesses of chlorine and of hydrogen, and of small proportions of ammonia, oxygen on the course, the rate of the reaction and its 'threshold potential'. The ionization current was found to diminish during the reaction and very large values obtained for the number of hydrochloric acid molecules produced *per ion*. The reaction was found to be explosive except with low pressures of the gas mixture and in the presence of a sensible excess of hydrogen.



## 25. Decomposition of hydrogen sulphide by electric discharge.

S. S. JOSHI and R. G. KHALSA, Benares.

The reaction has been studied under the spark and also silent discharge under different conditions of the applied potential, the gas pressure, the interelectrode distance, the frequency of the A.C. supply and so on. Hydrogen and free sulphur were the only products at any stage of the decomposition. The latter is produced in a peculiar grey form. The kinetics of its crystal growth under the discharge has been studied microscopically. Since the reaction does not produce any change of pressure, its course was followed by the analysis of the composition of the decomposition mixture at different stages. At a constant applied potential the percentage decomposition was found to diminish with the gas pressure in agreement with a theory developed by Elliott, Joshi and Lunt (*Trans. Farad. Soc.*, 1927, **23**, 57). The current varies in a characteristic manner during the progress of a given decomposition. It increased first rapidly and then slowly (latter depending upon the gas pressure) and finally became constant, with the completion of the decomposition. The 'threshold potential' decreased during the decomposition, presumably due to the diminution of hydrogen sulphide. Results are given for the M/F values under various conditions.

26. Raman spectrum of phenols from *Thymus serpyllum*.

B. SANJIVA RAO, Bangalore.

It was not found possible to determine by any known method a second phenol present in *Thymus serpyllum* oil, carvacrol being the main constituent. Raman spectrum of the different phenolic fractions has shown that the other phenol present is thymol.

## 27. Mechanism of inhibition of fluorescence.

K. S. GURURAJA DOSS, Bangalore.

A critical study has been made of the available experimental data on inhibition of fluorescence. On the assumption that inhibition is due to collisions of the second kind (cf. Jette and West, *Proc. Roy. Soc.* 1928, **A121**, 299) a formula has been obtained and found to explain quantitatively certain cases of inhibition brought about by ions. The autoinhibition of fluorescent substances, however, can satisfactorily be explained only on the basis of polymerization.

28. An X-ray investigation of the crystals of *p*-azotoluene.

MATA PRASAD and M. R. KAPADIA, Bombay.

The crystals of *p*-azotoluene belong to the monoclinic prismatic class, and the axial ratio found by the measurements of the interfacial angles is  $a : b : c = 2.1768 : 1 : 1.9674$ ;  $\beta = 90^\circ 16'$  (cf. Groth, V, p. 66). The X-ray study of the crystals has given the following lengths for the dimensions of the unit cell :

$$a = 12.00\text{\AA}, b = 4.851\text{\AA}, c = 9.703\text{\AA}.$$

These lengths have been found to give axial ratio which is in better agreement with that calculated from the interfacial angles measured by Groth. The unit cell belongs to the space group  $C_{2h}^5$  and contains two molecules. These facts show that the molecules in the unit cell have a centre of symmetry. The probable position of the molecules in the unit cell has been determined from the relative intensities of reflection of the observed planes.



29. A preliminary X-ray investigation of the crystal structure of hydroazobenzen.

JAGADISH SHANKER and MATA PRASAD, Bombay.

The crystals of hydroazobenzene belong to the bipyramidal class of the orthorhombic system. The axial ratio as obtained from crystallographical measurements is :

$$a : b : c = 0.9787 : 1 : 1.2497 \text{ (cf. Groth, V, p. 59).}$$

The crystals have been studied by the rotating crystal method. The dimensions of the unit cell are

$$a = 7.35\text{\AA}, b = 7.50\text{\AA}, c = 18.55\text{\AA}$$

which give the axial ratio in agreement with that recorded in Groth except that ( $c : b$ ) is doubled. The number of molecules per cell are found to be four. Since the least number of asymmetric units necessary to complete the symmetry of the point group  $Q_h$  is eight, the results indicate that there is some internal symmetry in the molecule inside the unit cell. The probable space group has been discussed. Intensity measurements are in progress.

30. An X-ray investigation of the crystals of (i) diphenyl disulphide, and (ii) diphenylene disulphide (thianthrene).

MATA PRASAD and B. H. PEERMAHOMAD, Bombay.

(1) The crystals of diphenyl disulphide belong to the rhombic system and crystallographic measurements give the ratio  $a : b : c = 0.6821 : 1 : 0.4987$  (cf. Groth, V, p. 33). The crystals were studied by the rotation and oscillation method. The dimensions of the unit cell are :

$$a = 8.10\text{\AA}, b = 23.84\text{\AA}, c = 5.61\text{\AA}$$

which shows that the ratios  $a : b$  and  $c : b$  are halved. The number of molecules per cell calculated from the dimensions of the cell and the specific gravity of the crystals (found to be 1.339) is four. The probable space group which would fit in with the observed halvings has been discussed.

(2) The crystals of thianthrene belong to the monoclinic prismatic class and

$$a : b : c = 3.7941 : 1 : 1.1807 ; \beta = 105^\circ 48'$$

(cf. Groth, V, p. 34). The X-ray rotation photographs give

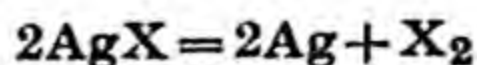
$$a = 22.86\text{\AA}, b = 6.0\text{\AA}, c = 14.66\text{\AA} ; \beta = 105^\circ 48'$$

which show that the ratio of  $c : b$  is doubled. The number of molecules per unit cell is eight. The molecules in the cell are asymmetric.

31. Photo-decomposition of silver halides.

S. S. BHATNAGAR, M. R. VERMA, and I. C. GUPTA, Lahore.

Magnetic susceptibility measurements of halides of silver at various stages of photo-decomposition under halogen absorbers like potassium nitrite, water, gelatine, carbon tetrachloride, etc. were carried out. The results suggest that the course of photodecomposition is represented by the equation :



where X is the halogen.



32. Transformation of chromic chloride in dilute solutions in the dark and ultra-violet light.

D. S. DATAR and M. QURESHI, Hyderabad (Deccan).

The transformation of the dark green chromic chloride in a 0.01 molar solution in the dark was followed by measuring extinction coefficient,  $P_{11}$  value and electrical conductivity at definite intervals of time. A state of equilibrium is reached in about six hours and a half. The peak of the absorption band of a freshly prepared solution lies at about 6400Å, while the position of maximum absorption in the case of the equilibrium mixture is near 5750Å. The results indicate that it is not a case of a simple and direct isomeric change of the dark green variety into the violet form, but that of a complex change taking place in several stages and accompanied by hydrolysis.

Exposure to ultra-violet light accelerates the rate of transformation.

33. Absorption spectra of binary liquid mixtures.

S. S. BHATNAGAR, P. L. KAPUR, and M. D. RAJPAL, Lahore.

The absorption spectra of mixtures of nitrobenzene and *o*-nitrotoluene with (a) aniline, (b) *o*-toluidine, (c) *m*-cresol, (d) toluene, and (e) *m*-xylene has been studied. As the nitro-bodies show general absorption in ultra-violet region even when present in small thicknesses the study has been restricted, therefore, to the visible region only. Binary mixtures of hydrocarbons with nitro-bodies give the superimposed spectrum of the components, of *m*-cresol with nitro-bodies show slight displacement and of amines with nitro-bodies exhibit large displacement of the absorption spectrum towards the red region. The slight displacement has been shown to be due to the dipolar association whereas the large shift has been attributed to the chemical association of the components.

34. Photo-electric threshold and latent heat of fusion.

B. N. SEN, Burdwan.

A formula has been proposed for the calculation of the photo-electric threshold wavelength from the latent heat of fusion of the metals concerned on the basis of Pauli-Sommerfeld theory of degenerate electron-gas for the metallic state with the modification that in the solid state the electrons cannot move in a force-free space and their mobility is governed by the least distance between the atoms. The formula may be represented thus :

$$\lambda_0 = k D \log (L)$$

where  $\lambda_0$  is the threshold wavelength,  $D$ , the distance of the closest approach of atoms,  $L$ , the latent heat of fusion and  $k$ , a constant depending upon the nature of the lattice.

The formula gives values in comparative agreement with those observed.

35. The melting points of mixtures of boric acid and hydroxylic substances.

S. M. MEHTA and (MISS) K. V. KANTAK, Bombay.

Boric acid was heated with mannitol, erythritol, glucose, galactose, tartaric acid and other hydroxylic substances until a clear melt was obtained. It was then sucked in a capillary tube where it was allowed to solidify. The melting point was determined according to the method of Christomanos (*Ber.*, 1890, 23, 1093). The amounts of boric acid and the hydroxylic substances were determined in a weighed portion of the melted



mass. When the melting points are plotted against the ratio boric acid : hydroxylic substance, curves are obtained which show that mannitol forms definite compounds with boric acid but that the other substances give melting point diagrams with eutectics which in certain cases are as low as  $60^{\circ}$ – $70^{\circ}\text{C}$ .

36. A rapid and accurate method of measuring the porosity of insulating materials.

B. S. SRIKANTAN, Waltair.

Insulating substances baked at different temperatures have different degrees of porosity. A quick and accurate method by the use of immersion pyknometer (*J.I.C.S.*, 1936, 13, 136) is described, in which by measuring the specific gravity and apparent density of these substances in a powdered form, the percentage of porous volume has been calculated.

37. Miscibility of alcohol and petrol.

S. R. BHATE and HABIB HASAN, Hyderabad.

The rapid increase in the production of molasses during the recent years is causing concern to sugar-producers. In most countries it is fermented and then used as motor fuel singly or in admixture with other suitable substances. The same suggestion is made in this paper and the strengths of alcohol which will freely mix with petrol have been worked out.

38. Viscosity of binary mixtures.

P. B. GANGULY and S. K. CHAKRAVERTY, Patna.

A relationship between viscosity of binary liquid mixtures and molecular association has been worked out. The expression has been tested in the case of the following systems: methyl alcohol, phenetole, acetic acid, acetone, linalool, phenol, benzyl alcohol, nitrobenzene, dissolved separately in benzene. In the majority of the cases studied the expression has been found to be applicable. The result has been discussed in the light of Hildebrand's idea of association (*J. Amer. Chem. Soc.*, 1916, 38, 1462).

39. Variation of surface tension with change in concentration of iodic acid solution.

M. R. NAYAR and A. B. SEN, Lucknow.

Surface tension values of the solute calculated from the mixture law equation give curves corresponding to the viscosity curves with the difference that the points of intersection become points of minima and the convex portions of the viscosity curve become concave here. The points of intersection are 0.04N and 0.1N. Parachor values are being calculated.

40. Kinetics of reactions in heterogeneous systems. Part III. Hydrolysis of esters.

D. D. KARVE and V. L. MEHENDALE, Poona.

The velocity of hydrolysis of (a) benzyl acetate and (b) benzyl propionate with dilute solutions of hydrochloric acid have been studied at room temperature, the ester being dissolved in xylene. The effect on the velocity of hydrolysis of changes in the concentrations of the hydrochloric acid and of the ester respectively, of increase in the quantities of the acid used and of the addition of a neutral salt have been studied.



41. Kinetics of reactions in heterogeneous systems. Part IV.  
Velocity of hydrolysis of some aromatic acid halides.

D. D. KARVE and K. K. DOLE, Poona.

The velocities of hydrolysis by water of benzoyl chloride, cinnamyl chloride and of benzoyl bromide dissolved in monochlorobenzene were studied under varying conditions of concentration of the reacting substances. The velocity constants calculated according to the monomolecular formula have given fairly constant values.

42. Kinetics of the reaction between chloral hydrate and sodium hydroxide.

A. N. KAPPANNA, Nagpur.

A detailed study of the kinetics of the reaction has been made. The bimolecular velocity constant varies with the initial concentrations of the reactants. A mechanism for the reaction, to account for the observed results, has been suggested.

43. Kinetics of heterogeneous organic reactions: A study of the benzoin reaction.

B. F. FERREIRA and T. S. WHEELER, Bombay.

In the study of the kinetics of the benzoin reaction at 80° the curves obtained with 1, 2 and 3 gms. of potassium cyanide are similar to those obtained at 100°C (Parts I and II, *J. Phys. Chem.*, 1935, 39, 727) but the reaction is much slower at the lower temperature. The reaction is also being studied at 70° and 90°. Owing to the sensitiveness of the reaction to inhibitors difficulty has been experienced in obtaining consistent results at the lower temperatures.

It has been confirmed by means of long period adsorption experiments with small quantities of potassium cyanide that the benzaldehyde hitherto used in all the experiments was of a standard degree of purity (cf. Part V, *Proc. Ind. Acad. Sci.*, 1935, 2, 605).

44. A study on the velocity of hydrolysis of some aromatic nitriles.

D. D. KARVE and D. V. GHARPURE, Poona.

Benzonitrile, *o*- and *p*-tolunitriles and benzyl cyanide were hydrolysed by known strengths of sulphuric acid using glacial acetic acid as solvent. The quantities of amide and ammonium salts formed were estimated separately and the total quantity of cyanide hydrolysed was calculated. The effect on the velocity of hydrolysis of the concentration of the sulphuric acid is being studied. It is also seen that owing to steric hindrance, *o*-tolunitrile remains practically unhydrolysed after 2.5 hours at 100° with 16.34N sulphuric acid.

45. Influence of temperature and of foreign electrolytes on the partition co-efficient of iodine between toluene and water.

S. S. JOSHI and R. R. GOREY, Benares.

The above constant has been measured in the temperature range 10–40°C and in the presence of different amounts of KI, KCl, NaCl and LiCl. Definite evidence is obtained from these data for the occurrence of polyhalides with the above named constituents under these conditions.



From a knowledge of the shift of the mass law co-efficients characteristic of these complexes, approximate estimates have been made of the corresponding heats of formation.

46. System : Sulphuric acid—ethers.

S. K. K. JATKAR and N. G. GAJENDRAGAD, Bangalore.

Sulphuric acid can be used to absorb the vapours of methyl and ethyl ether and the ether subsequently recovered by adding water and distilling. It is very important to know in what form the ether is absorbed and how much of it can be theoretically recovered. A continuation of the previous study of the viscosity and conductivity of the mixtures of ether with sulphuric acid has shown that although the additive compounds  $\text{H}_2\text{SO}_4 \cdot \text{C}_2\text{H}_5\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  are formed (which can give up ether on addition of water) mixtures of pure sulphuric acid and small quantities of ether, give rise to further chemical reactions resulting in the formation of water. This fact alone explains quantitatively the maxima in the conductivity-composition curve and the displacement of the maxima from that required for the two above additive compounds, in the viscosity-composition curve. A limit is therefore set to the amount of ether recoverable by this process. This study has been extended to the systems sulphuric acid—methyl ether and sulphuric acid—propyl ether.

47. Equilibrium in the system  $\text{K}_2\text{CrO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$ .

S. GOPALA RAO and K. R. KRISHNASWAMI.

The various solubility determinations and the compositions of the equilibrium mixtures relating to the above system at different temperatures were carried out in a thermostat by a method described in detail in the paper.

The tables given in the paper show the results obtained.

48. Valve potentiometer.

S. K. K. JATKAR, Bangalore.

This paper describes the various valve circuits used in the potentiometric investigations in our laboratory : (1) one electrometer triode followed by one stage D.C. amplifier using  $\text{LP}_2$ , a Unipivot galvanometer serving as the indicating instrument, (2) two electrometer triodes in push pull using a mirror galvanometer as a null instrument, (3) one electrometer valve followed by two stages of resistance capacity coupled amplifier, using a ballistic galvanometer as a null instrument, and (4) two  $\text{P}_2$  valves in push pull for use both as a voltmeter for measuring pH and for differential electrometric titration, a unipivot galvanometer being the indicating instrument. The grid current is reduced to less than  $10^{-11}$  amp.

49. Automatic potentiometric titration.

S. K. K. JATKAR and C. T. ABICHANDANI, Bangalore.

In view of the long time taken in electrometric titrations we have developed a simple apparatus for automatically recording the titration curve of both  $E$  and  $dE/dc$  against c.c. The reagent is added by the continuous movement of a cylindrical graduated plunger, released by the recording drum which is moving at a controlled speed. The electrodes are connected to a push pull vacuum tube circuit having a mirror galvanometer between the two anodes. The movement of the spot of light was either hand-recorded on a Cambridge Curve Tracer or photographed on a bromide paper.



50. Electrode potential of tungsten, tantalum, platinum, nickel, antimony, silver and silver chloride electrodes.

C. T. ABICHANDANI and S. K. K. JATKAR, Bangalore.

In the course of our experiments on the suitability of a bimetallic electrode systems for the electrometric titration of acids and bases, we studied various electrodes such as W, Ta, Pt, Ni, Sb, Ag and Ag-AgCl in buffers of different pH values.

Antimony behaves abnormally after 8 pH while tungsten behaves very well up to 10 pH. It is further observed that Ag-W, Pt-W, Ag-Sb and Pt-Sb are good pairs for the electrometric titration of acids and bases.

The tungsten electrode was used by us for the differential titration of acids and bases and it gave very sharp end points. The electrode was a wire of tungsten 1 mm. thick. We polished the electrode with sand paper at the commencement of each operation and found that the polished electrode behaved more like a hydrogen electrode than the tarnished or oxidised electrode. This behaviour is similar to that of antimony electrode.

Further the E.M.F. of the cell W (polished)/solution/H<sub>2</sub> was found to be almost constant at different pH values, showing that the polished electrode behaves more like a hydrogen electrode. The temperature co-efficient of the above electrode system was found to be .003 volt.

51. Potentiometric titration of aromatic bases.

C. T. ABICHANDANI and S. K. K. JATKAR, Bangalore.

The differential titration of aromatic bases such as pyridine,  $\alpha$ -picoline,  $\beta$ -picoline, quinoline, quinaldine and isoquinoline by hydrochloric acid was carried out using polished tungsten wires as electrodes.

The double peaks obtained for the end points are in favour of the idea of the existence of Kekule isomers of some of these compounds.

52. Electrolysis of aqueous calcium chloride. Part I.

S. S. JOSHI and S. P. SARKAR, Benares.

This has been studied in respect of the influence of (a) temperature, (b) nature of the electrode materials, (c) current density, (d) composition of the liquor at different stages of the electrolysis, and (e) initial addition of free HCl, K<sub>2</sub>CrO<sub>4</sub> and other materials. Conditions have been studied for the non-ignition of calcium liberated at the cathode and its isolation by use of metallic mercury under special conditions. The electrolysis increases very appreciably the proportion of available chlorine, chiefly through the hypochlorite formation. The concentration of the product reaches a steady value after a certain period, whereafter, that of the chlorate begins to rise except when the temperature is too low. The addition of but small amounts of K<sub>2</sub>CrO<sub>4</sub> has been found to have marked influence in increasing the yield of the hypochlorite.

53. Transport number of the silver ion in the presence of methyl alcohol.

S. S. JOSHI, A. J. HARI RAO, and K. RAMADAS, Benares.

It has been observed that the transport number of the silver ion increases to a maximum as the proportion of methyl alcohol in the mixture is increased, and then diminishes for further increase of methyl alcohol. Determinations of the viscosity of the medium at different percentages of methyl alcohol gave curves strikingly similar to those obtained in respect of the transport numbers. These results are discussed on the possible variations of the significant ionic mobilities, formation of com-



plexes between the two components, hydration of the ions and other possible determinants of the transport number, on the basis of the theories developed by Kruger (*Z. Elektrochem.*, 1916, **22**, 445), Krumarisch (*ibid.*) and others.

54. Aqueous solutions of sodium aluminate.

S. M. MEHTA and (MISS) OLIVE JOSEPH, Bombay.

Solutions containing different proportions of sodium hydroxide and aluminium hydroxide expressed as the ratios of  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$  have been investigated in the same manner as those of sodium zincate reported before (*Proc. Ind. Sci. Cong.*, 1935, p. 113) by one of the authors. The electrical conductivity has been measured between 2N and 0.01N. Crystals of definite aluminates have been isolated from the solutions containing hydroxide dissolved in more than 10N sodium hydroxide as well as from those in 2N and 5N sodium hydroxide. Further work on the determination of the hydrogen ion concentration by means of the glass electrode is in progress.

55. Electro-typing.

V. MANIYAN, Bangalore.

The suitability of different wax mixtures for getting accurate impressions from old coins and of different preparations of graphite for coating the impressions prior to electrotyping, has been investigated.

56. The evaluations of  $\Lambda_0$  and of  $K$  for soaps in alcohol-water mixtures.

S. K. K. JATKAR and B. S. V. K. VITTAL, Bangalore.

In continuation of our previous study of the conductivity of pure soaps in ethyl alcohol and ethyl alcohol-water mixtures, we have now calculated  $\Lambda_0$  the limiting conductance, and  $K$  the dissociation constant by the method of Fuoss and Kraus, for all the mixtures except 87 per cent. alcohol which is anomalous because the conductance decreases with dilution in the same range in which there is an increase in the case of other mixtures.

57. The influence of magnetic field on adsorption.

S. S. BHATNAGAR, P. L. KAPUR, and A. N. KAPUR, Lahore.

Effect of magnetic field on the adsorption of  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{FeCl}_3$  by charcoal and of  $\text{KMnO}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  by  $\text{BaSO}_4$  has been studied. In the system  $\text{KMnO}_4$ -charcoal  $\text{K}_2\text{Cr}_2\text{O}_7$ -charcoal adsorption is increased; in  $\text{FeCl}_3$ -charcoal it is decreased; whereas in  $\text{KMnO}_4$ - $\text{BaSO}_4$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ - $\text{BaSO}_4$  it is not influenced by magnetic field.

Thus we find that magnetic field influences adsorption as it does various other chemical reactions according to rules deduced by Bhatnagar, Mathur and Kapur (*Phil. Mag.*, 1929, **8**, 457).

58. Particle size and magnetic susceptibility.

S. S. BHATNAGAR, M. R. VERMA, and M. ANWAR-UL-HAQ, Lahore.

The mass magnetic susceptibility of lead, copper, bismuth, antimony, sulphur, selenium and tellurium has been measured at particle size of the order  $0.4\mu$  and has been found in each case to be the same as that of the



corresponding metal *en masse*, provided impurities like oxides, hydroxides, carbonates, etc. are suitably removed. Evidence in favour of this point has also been brought forth by agglomerating the purified powder of lead, bismuth and antimony, when no change in the susceptibility value is observed, which it should have been if there were any particle size effect.

It is pointed out that Rao's conclusions (*Current Science*, 1936, 4, 572) on copper, bismuth and antimony are not correct because he has presumably neglected the influence of carbon inclusion in the case of the former metal and that due to the formation of oxides and hydroxides in the case of the last two metals. Further, his inference from the work of Prins that antimony is amorphous in the colloidal state is not borne out from the original text of Prins.

### 59. Magneto-optical rotation of liquid mixtures.

S. S. BHATNAGAR, M. R. VERMA, and P. C. KHANNA, Lahore.

Magneto-optical rotation of the following pairs of liquids was measured at various molar concentrations :—

- (1) Xylene—aniline, (2) Toluene—aniline, (3) Xylene—nitrobenzene, (4) Xylene—*o*-nitrotoluene, (5) Toluene—nitrobenzene, (6) Nitrobenzene—aniline, (7) Aniline—*m*-cresol, (8) *o*-Nitrotoluene—*m*-cresol, (9) Nitrobenzene—*m*-cresol, (10) Water in phenol—phenol, (11) Phenol in water—water.

Deviation in rotation from the additivity value is obtained only in those mixtures which show a departure in density from the linear law. The results are discussed in view of the possibility of dipolar association and chemical combination.

### 60. A magnetic study of colour changes in cobalt chloride.

S. S. BHATNAGAR, A. N. KAPUR, and P. L. KAPUR, Lahore.

Magneto-optic rotations of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  solutions in different solvents have been studied. The colour and molecular magnetic rotation of cobaltous chloride solutions in amyl alcohol and hydrochloric acid change considerably with concentration while in aqueous solutions the change is only just noticeable. The colour change is brought about both by changing the state of ionization and by causing dehydration, but the predominant factor is the formation of complex ions of the type  $(\text{CoCl}_3)^-$  and  $(\text{CoCl}_4)^{2-}$  as already suggested by Bhatnagar and Kapur (*J. Indian Chem. Soc.*, 1932, 9, 341).

### 61. Decolourising action of fuller's earth.

B. S. KULKARNI and S. K. K. JATKAR, Bangalore.

In the course of the work on the activation of Fuller's earths obtained from different parts of India, it was observed that the pH of the solution of sodium chloride treated with the earths varied in the same manner as the change in the units of colour removed. It has been found that the decolourising action and the activation of these earths by acids are directly related to the exchangeable hydrogen ions contained in the earths. Thus the cation of the Fuller's earth which is of zeolitic nature is replaced by the hydrogen ion during the process of activation by acids, the hydrogen in turn being replaced by sodium ion when treated with the salt solution, both reactions being governed by law of mass action. This paper reports the results obtained regarding the value of the equilibrium constant involved for the different earths studied.



62. Effect of ultra-violet light on chromium hydroxide sols of a high degree of purity.

D. S. DATAR and M. QURESHI, Hyderabad (Deccan).

Chromium hydroxide sols were prepared by three different methods and purified by the process of continuous dialysis extending over 60 hours and more. The progress of dialysis was followed up by the measurement of light-absorption, pH value and electrical conductivity. The extinction co-efficient curves of the dialysed sols have the same form and the same regions of maximum and minimum absorption namely 5900 and 5150Å, respectively, although the intensity of absorption in each case is different.

Exposure for 24 hours to ultra-violet light of a sol dialysed for 60 hours, results in an increase in the light-absorption as well as in the chromium-chlorine ratio. The pH value shows at first a decrease, followed by an increase on long exposures. Similarly electrical conductivity first decreases and then increases. An explanation has been offered for this behaviour. The effect of dilution and ageing on the abovementioned properties has also been investigated.

63. On the relation between peptisation of a precipitate and its electrokinetic potential and the electric charge of a precipitate formed in presence of an excess of one of the constituent ions.

S. G. CHAUDHURY and J. SEN GUPTA, Calcutta.

During the course of peptization of a precipitate, a rise of the electric charge of the particles of the precipitate always occurs. The precipitates studied are copper ferrocyanide, uranium ferrocyanide, zinc ferrocyanide and silver iodide. A polar precipitate does not always show a positive charge in presence of an excess of an electrolyte having a constituent positive ion, nor does it always show a negative charge in excess of an electrolyte having a constituent negative ion.

The charge of a polar precipitate in excess of either one or other electrolytes taken for precipitation depends: (a) on the initial concentrations of the precipitants taken, and (b) on the time after which measurements of charge were taken, i.e., on the age of the precipitate. These observations go against all the theories hitherto proposed to explain the nature of the charge of a polar precipitate in presence of an excess of either of the common ions.

The work was undertaken under the guidance of Prof. J. N. Mukherjee.

64. Colloidal structure and infra-red absorption spectra.

S. S. BHATNAGAR, P. L. KAPUR, and M. D. RAJPAL, Lahore.

Infra-red absorption spectra of  $\text{Fe}_2\text{O}_3$ ,  $\text{As}_2\text{S}_3$ ,  $\text{SiO}_2$ ,  $\text{SnO}_2$  and Au hydrosols prepared by different methods has been studied between  $0.8\ \mu$  and  $2.0\ \mu$ . Almost all the sols have been found to be less transparent than water in the region of  $0.9\ \mu$  to  $1.3\ \mu$  and  $1.55\ \mu$  to  $1.75\ \mu$  and are more transparent in the region  $1.3\ \mu$  to  $1.55\ \mu$  and beyond  $1.75\ \mu$ . There is a striking similarity between their percentage transmission curves particularly in respect of the absorption bands occurring at  $1.0\ \mu$ ,  $1.2\ \mu$  and  $1.6\ \mu$ . The change in transparency of water and the shifts in the position of water bands has been attributed to the disturbance of equilibrium between the mono-, di- and trihydrol molecules of water caused by the hydrated colloidal particles. The  $\text{SiO}_2$  and  $\text{SnO}_2$  sols have been shown to have maxima of the absorption bands at  $1.26\ \mu$ ,  $1.9\ \mu$  and  $1.06\ \mu$  respectively besides those of the other sols. This difference in two sets



of sols is due to their difference in nature, i.e., their hydrophobic and hydrophilic character.

65. 'Zonal effect' in the variation of the opacity during the coagulations of colloid manganese dioxide.

S. S. JOSHI and P. V. JAGANNATHA RAO, Benares.

That coagulation leads necessarily to an increase of the turbidity or opacity of the coagulating system has been assumed tacitly by colloid chemists. This underlies the numerous investigations on the kinetics of the above process from an experimental standpoint, in the light of the current theories developed chiefly by Smoluchowski (*Z. physikal. Chem.*, 1917, **92**, 129), Freundlich (*Colloid and Capillary Chemistry*, 1926, pp. 442) and others. As is to be anticipated from the simple and restricted mechanism of the process contemplated in the above theories, disparity exists appreciably between the requirements of the theory and actual practice, especially in the slow region of the reaction. Based on the results of work from these laboratories, it was suggested that the change is essentially discontinuous as revealed in the time variation by some of the principal properties which are employed usually by following the progress of coagulation. No information in this line is available in the literature in respect of the opacity as a measure of the change. With the exception of two preliminary communications (Joshi and Jaya Rao, *J. Indian Chem. Soc.*, 1936, **13**, 311; Joshi and Purushottam, *Current Science*, 1936, **4**, 870), it does not appear to have been noted that even this property, which has had perhaps longest and widest usage as a measure of coagulation, shows a 'zonal effect' in the slow region. More detailed studies have shown in the case of colloidal manganese dioxide using differently concentrated solutions of KCl, BaCl<sub>2</sub> and CH<sub>3</sub>COOH as coagulants that, contrary to usual experience, the opacity actually diminishes after the familiar rise in the initial stages. Under certain conditions the opacity diminishes first and then rises. Interesting results were obtained when monochromatic light was used for the opacity measurements. Under all these conditions, it was found that the change of opacity was always zonal irrespective of whether this property changed normally or otherwise during the occurrence of the change.

66. 'Zonal effect' in the coagulation of gold hydrosol.

S. S. JOSHI and N. HANUMANTHA RAO, Benares.

In previous communications from these laboratories (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329; Joshi and Menon, *ibid.* 1933, **10**, 599; Joshi and Nanjappa, *ibid.*, 1934, **11**, 133; Joshi and Iyengar, *ibid.* 1934, **11**, 555; 573; 577; Joshi and Pannikar, *ibid.* 1934, **11**, 797, 804; 1936, **13**, 309; *Proc. Acad. Sci. U.P.*, 1935, **5**, 41; *J. Chim. Phys.*, 1935, **32**, 455; Joshi and Sarkar, *J. Bombay Univ.*, 1935, **4**, 140; Joshi and S. Jaya Rao, *J. Indian Chem. Soc.*, 1936, **13**, 141; 311; *Koll. Zeit.* 1936, **76**, 146), it has been shown that the process of slow coagulation of a number of sols produced by variously concentrated solutions of different electrolytes, and by oppositely charged sols is not continuous with respect to the coagulation time. Since this conclusion constitutes a departure from the current theories of the kinetics of coagulation, it was of interest to follow the coagulation of gold hydrosol, for which very detailed data are available in the literature.

In the present work, two independent methods were employed to follow the process of coagulation, viz. change of the viscosity and of refractive index. These experiments show that coagulation is not time-continuous and that this feature becomes more pronounced the slower the change. Results also show, contrary to the tacit assumption made generally by colloid chemists, that coagulation does not necessarily produce a net increase of viscosity. Moreover, contrary to the finding



of Galecki (*Koll. Zeit.*, 1925, 36, 154, et. seq.) the characteristic changes, viz., red to violet, is not confined to the occurrence of the first minimum on the viscosity—time curves. The discontinuities termed the 'Zones of coagulation' are brought out vividly by the refractivity—time curves which have been studied in detail. The 'zones' tend to disappear during both rapid and very slow coagulations.

67. The coagulation of colloid antimony sulphide by aqueous mercury chloride.

S. S. JOSHI and T. MADHAVA MENON, Benares.

It was shown in a recent publication (Joshi and Kulkarni, *J. Indian Chem. Soc.*, 1936, 13, 439) that in by far the majority of cases coagulations of colloid arsenious sulphide produced no sensible variations in the viscosity, transparency and opacity (determined by independent means) of the colloid when coagulated by mercury chloride. The normal variations in these properties occurred under the above conditions if other electrolytes were used as coagulants both when (i) used alone, and (ii) when but small amounts of these were mixed with  $\text{HgCl}_2$  used for producing coagulation. These measurements have now been extended to the study of the coagulation of colloid  $\text{Sb}_2\text{S}_3$  by  $\text{HgCl}_2$ . It was found that the character of the variation of any of the above properties depended chiefly upon the coagulator concentration. For low values of the latter, results were similar to those obtained in the case of colloid  $\text{As}_2\text{S}_3$  and  $\text{HgCl}_2$ , in respect of all the three properties mentioned above, i.e., they remained sensibly stationary although visible flocculation had occurred in the system. In rapid coagulations all the properties showed the familiar type of variation. In intermediate regions, all the properties showed discontinuous variations. This last conclusion was also confirmed by a detailed study of the change of refractive index during coagulation. It is concluded, therefore, that the *ad hoc* utilization of any of these four properties as a measure of the corresponding degree of coagulation is subject to an inherent uncertainty. It is certainly unreliable as a general measure of coagulation.

68. Viscosity of thorium molybdate gels during formation.

MATA PRASAD and (MISS) RATHNAMA, Bombay.

The viscosity of thorium molybdate gels prepared by mixing solutions of thorium nitrate and potassium molybdate has been measured at different intervals during its formation. The effect of the variation of concentrations of thorium nitrate and of potassium molybdate and of the addition of electrolytes and non-electrolytes on the viscosity of the gel-forming mixtures has also been examined. The viscosity—time curves are irregular. The thiotropy of these gels is discussed in view of these observations. All the gels used in this investigation were transparent or translucent.

69. Swelling of gels. Part II.

N. A. YAJNIK and M. AHZAL KHAN, Lahore.

The swelling of blue and agar-agar gels in water has been studied at various pH's and in presence of different electrolytes. It has been observed that :

1. In case of glue gels the swelling was minimum at pH 5, while in agar-agar gels the maximum imbibition was obtained at pH 7.
2. On comparing the influence of the electrolytes with common anions, it was observed that the swelling of glue gels went on decreasing with the increase of molecular weight, whilst reverse was the case of agar-agar gels.



## 70. Studies in barium malonate gels.

MATA PRASAD *and* KARTAR NARAIN, Bombay.

The setting of barium malonate gels has been studied at different temperatures using solutions of different concentrations of the malonic acid. It has been found that with an increase in the concentration of the acid the time of setting first decreases, reaches a minimum, then increases and reaches a maximum and again decreases until at high concentrations the time—concentration curve runs almost parallel to the concentration axis. The increase of temperature also shows that the time of setting first increases, reaches a maximum value and then decreases.

## 71. Studies in inorganic gels.

MATA PRASAD *and* D. M. DESAI, Bombay.

A number of inorganic gels, some already known, have been obtained in a transparent condition by properly controlling the hydrogen-ion concentration of the gel forming mixtures. In each case the limits of concentration of the gel-forming solutions have been determined and the effect of temperature and of the addition of non-electrolytes on the formation of gels has been examined. The heat of activation of the gels has been calculated from Arrhenius' equation.

## 72. Adsorptive properties of synthetic resins.

S. S. BHATNAGAR, A. N. KAPUR, *and* M. L. PURI, Lahore.

Adsorptive properties of synthetic resins have been studied in detail and the authors find that the taking up of dissolved substances from solution by the adsorbent resins follows the ordinary laws of adsorption and is mainly a surface phenomenon. The adsorption from aqueous solutions of benzoic, salicylic, anthranilic, picric, formic, acetic, propionic, butyric, amino-acetic, lactic, sulphuric, nitric, hydrochloric acids has been studied. Aromatic acids are adsorbed to a greater extent than aliphatic acids. In a homologous series, the adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the series. Inorganic acids are preferentially adsorbed in the order  $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$ . The adsorption from solutions other than aqueous was also studied and the use of difference in degree of sorption from solvents in the recovery of various substances from solutions has been investigated. These resins can be economically prepared as commercial adsorbents and have advantage over charcoal and silica in that, whereas charcoal does not adsorb inorganic bases and silica inorganic acids, the resins adsorb both types of substances fairly strongly.

## 73. Adsorption by precipitates.

N. A. YAJNIK, P. L. KAPUR, *and* R. L. MALHOTRA, Lahore.

Adsorption of various negative ions namely oxalate, ferro-cyanide, iodate, chromate, nitrate, cyanide, chloride, permanganate, bromate and sulphocyanide by iron, aluminium, chromium and manganese hydroxides has been studied. The hydroxides, precipitated at the ordinary temperature from corresponding 2N-chloride solutions by dilute ammonia, were washed by decantation and dialysed till free from chloride. Known weight of the hydroxide was always taken and the conditions for adsorption of different ions were kept the same. The order of the ions adsorbed is :

oxalate > ferrocyanide > iodate > nitrate > chromate > cyanide >  
chloride > permanganate > bromate > sulphocyanide.



## Organic Chemistry

## 74. Dehydrogenation of methanol.

N. V. KAREKAR and S. K. K. JATKAR, Bangalore.

We have measured the comparative activity of different catalysts like copper, brass, silver plated copper guage and calcium silicate-vanadate, for dehydrogenating methanol to yield formaldehyde. The last named catalyst was found to be the best.

## 75. Constitutions of 'Urea' from chemical reactions and physico-chemical studies.

P. B. SARKAR, B. C. RAY, and J. GUPTA, Calcutta.

Although the literature on the subject seems exhaustive, and various views have been put forward—*singly* none of them appears to be satisfactory. The 'chemical' constitution, may or may not be identical with the 'true' constitution of a compound. They are identical, however, only where mobility and reversibility are exceptional. The problem of this nature cannot be solved by examining the behaviour in solution. Examination of the solid is essential. Physico-chemical methods have been applied to arrive at a reconciliation of the various facts hitherto observed.

76. Studies in geometrical isomerism. Part IV. The action of organic bases on  $\alpha$ -bromo-lignoceric acid and its methyl ester.

P. RAMASWAMI AYYAR, Bangalore.

The action of dimethylaniline on the bromo-acid yields the expected  $\Delta 2:3$ -unsaturated acid, the geometrical isomerism of which is under investigation. But the action of pyridine on the methyl ester gives a yellow condensation product (m.p.  $185^\circ\text{d}$ ) which is under investigation.

77. Studies in geometrical isomerism. Part V. The action of diethylaniline on  $\alpha$ -bromo-stearic acid and its methyl ester.

(MISS) P. DEVI and P. RAMASWAMI AYYAR, Bangalore.

The remarkable observation has been made that stearic acid is a product of the above reaction, in addition to the expected  $\Delta 2:3$ -oleic acid, the geometrical isomerides of which are being investigated.

78. Studies in geometrical isomerism. Part VI. The action of bases on  $\alpha$ -bromo-eicosanic acid.

(MISS) P. DEVI and P. RAMASWAMI AYYAR, Bangalore.

The action of methyl alcoholic and ethyl alcoholic potash on the bromo-acid yields only  $\alpha$ -hydroxy-eicosanic acid, and not the expected  $\Delta 2:3$ -eicosenoic acid. The action of diethylaniline on the bromo-acid and its methyl ester is being studied.



79. The condensation of aldehydes with malonic acid in the presence of organic bases. Part VIII. The condensation of methoxy-salicylaldehyde.

K. C. PANDYA and T. A. VAHIDY, Agra.

Methoxy-salicylaldehyde was condensed in the usual way, by the method of Kurien and Pandya (*J. Indian Chem. Soc.*, 1925, 11, 825) and Pandya and Vahidy (*Proc. Ind. Acad. Sci.*, 1935, 2, 402), with malonic acid in the presence of a trace of pyridine, piperidine, lutidine, etc. Quantitative yields of *o*-methoxycinnamic acid were obtained.

It may be noted that *m*-methoxy-benzaldehyde has similarly been condensed to give *m*-methoxycinnamic acid in 90 per cent. yield by the same method by Robinson and Walker (*J.*, 1936, 193).

80. Quantitative determination of aromatic amines. (Application of the potentiometric method to diazotization).

BALWANT SINGH, G. AHMAD, and H. B. DUNNICLIFF, Lahore.

*o*-Nitroaniline, *m*-nitroaniline, *p*-nitroaniline, *o*-aminobenzoic acid, *p*-aminobenzoic acid, sulphanilic acid, *p*-chloroaniline, 3-nitro-4-aminophenetole and 2-amino-4-nitrophenol have been determined quantitatively by titrating them against a standard solution of sodium nitrite in presence of hydrochloric acid by the potentiometric method.

81. Reactivity of piperonyl halides.

R. G. NAIK and T. S. WHEELER, Bombay.

The authors have studied the reactivity of the side-chain halogen atom in various piperonyl halides. The halogen atom in the side-chain is easily replaced when refluxed with alcohols in presence of sodium carbonate giving the corresponding ethers. If the alkali be not present, polymerization occurs.

The halogen atom in the side-chain is easily replaced by the cyano-group, when refluxed with alcoholic potassium cyanide for several hours. The nitriles on hydrolysis with alkali readily yield the corresponding phenyl-acetic acids. This new method of synthesising phenyl-acetic acids appears to be of interest.

82. Imido-chlorides: Condensation of N-methylurethane with benzanilideimidochloride.

R. C. SHAH and H. P. GHADIALI, Bombay.

In view of the interesting results obtained with N-phenylurethane (*Indian Sci. Cong. Abst.*, 1936, 101), the investigation has been extended to N-methylurethane. The crystalline condensation product phenyliminobenzyl-methyl-urethane is readily hydrolysed by boiling dilute hydrochloric acid to benzanilide, and forms a stable dibromo additive product. Phenyliminobenzyl-methylurethane, like the corresponding N-phenyl compound, does not undergo cyclization to a quinazoline derivative; the N-methyl group, like the N-phenyl group therefore inhibits ring-closure. The action of alcoholic potash led to phenylmethyl-benzamidine. The action of  $\alpha$ -naphthylamine gave a urea derivative, and reduction by aluminium amalgam in moist ether afforded the dihydro-compound which is readily hydrolysed to benzaldehyde.



## 83. Studies in the chemistry of amidines : Diamidines.

H. K. S. RAO and T. S. WHEELER, Bombay.

Dibenzoyl benzidine and  $\text{PCl}_5$  react in the presence of nitrobenzene to give the corresponding di-imidochloride. This has been condensed with aryl amines and ammonia to give di-amidines all of which are new. The imidochloride has been condensed so far with monomethyl-aniline, mono-ethylaniline, ethyl-*p*-toluidine, ethyl-*o*-toluidine, methyl-*o*-toluidine, benzyaniline, *o*-chloraniline, *o*-anisidine, *o*-toluidine and ammonia. All these amidines which are yellow crystalline solids with very high melting points, have been converted into picrates.

The imidochloride resulting from the reaction of  $\text{PCl}_5$  on dibenzoyl-*p*-phenylenediamine in the presence of nitrobenzene, has been condensed with aryl amines to give the corresponding di-amidines. The amines so far used are methylaniline, methyl-*o*-toluidine and benzyaniline. The amidines are being converted into picrates and hydrochlorides.

It is hoped eventually to study the tautomerism of the di-amidines.

## 84. Geometrical isomerism in amidines.

R. C. SHAH and M. M. SIDIKI, Bombay.

The isomerism of the two pairs of amidines obtained from benzanilide-imidochloride by the action of: (i) monomethylaniline and dimethylaniline, and (ii) monoethylaniline and diethylaniline (*J.*, 1932, 649) has been further studied. The constitutions of the amidines as *N*-alkyl diphenylbenzamidines—(a) *N*-methyl, (b) *N*-ethyl—have been established by hydrolysis with conc. hydrochloric acid in a sealed tube at a high temperature, and also confirmed by molecular weight determinations. The isomerism is, therefore, most probably geometrical isomerism. This observation is of interest as geometrical isomerism has not been hitherto encountered in the amidine series.

85. Condensation of  $\beta$ -aryl glutaconic acids with phenolic ethers.

G. R. GOGTE, Bangalore.

The constitution viz.  $\beta\beta$ -(4 : 4'-dimethoxy-diphenyl)-glutaric acid assigned to the product of condensation of  $\beta$ -(4-methoxyphenyl)-glutaconic acid with anisole reported last year (*Proc. Ind. Sci. Cong.*, 1936, 24) has been proved conclusively by the formation of the well known  $\alpha\alpha$ -(4 : 4'-dimethoxy-diphenyl)-ethylene from the latter on treatment with lime.

The  $\beta$ -(4-ethoxyphenyl)-glutaconic acid, the  $\beta$ -(4-methoxy-3-methyl)-glutaconic acid and the  $\beta$ -(4-ethoxy-3-methyl)-glutaconic acid, condensed in a similar manner with phenetole, *o*-cresol-methyl and ethyl ethers respectively to give the corresponding  $\beta\beta$ -diaryl glutaric acids of the para-series. These latter also produced the corresponding  $\alpha\alpha$ -diaryl ethylenes by lime treatment.

## 86. Halogenation. Part XX. Halogenation of fluorene.

P. S. VARMA and V. SUBBA RAO, Benares.

From the study of the literature it seems that only one iodo-derivative of fluorene has been obtained before and no mixed halogen derivatives are known. It has been possible to prepare a second derivative of fluorene, 2 : 7-di-iodofluorene, by three different methods; the one from 2 : 7-dinitrofluorene by reduction and diazotization, the second from 2-iodo-fluorene by nitration, reduction and subsequent diazotization and the third from fluorene itself by direct iodination in presence of strong nitric and fuming



sulphuric acids. All the three methods yield the same di-iodo-derivative. A number of new mixed halogen derivatives such as bromo-iodo-fluorene, chloro-bromo-fluorene, bromo-iodo-fluorene etc. have also been prepared.

87. Halogenation. Part XXI. Bromination and iodination of triphenylmethane.

P. S. VARMA and V. RAMA IYER, Benares.

The study of the literature shows that little work has been done on the direct bromination and iodination of triphenylmethane. Most of the bromo- and iodo-derivatives have been obtained by indirect methods only. Triphenylmethane has been brominated by the authors under different conditions in the cold or on a water bath in presence of substances such as (I) concentrated nitric acid, (II) fuming nitric acid, (III) concentrated sulphuric acid, (IV) fuming sulphuric acid, (V) a mixture of strong nitric and sulphuric acids, (VI) a mixture of fuming nitric and fuming sulphuric acids, and (VII) sodium nitrite and fuming sulphuric acid and a number of bromo-derivatives obtained. The conditions for getting the maximum yield of these compounds have also been studied. Similar experiments have also been conducted on the direct iodination of triphenylmethane.

88. Halogenation. Part XXII. Halogenation of methylethylaniline.

P. S. VARMA and P. V. ANANT RAMAN, Benares.

An exhaustive study of the chlorination, bromination and iodination of methylethylaniline has been made and a number of chloro-, bromo- and iodo-derivatives have been obtained. Some of these halogen derivatives have also been nitrated and some new nitro-halogen derivatives have been prepared.

89. Halogenation. Part XXIII. Halogenation of monomethyl-*o*-toluidine.

P. S. VARMA and D. B. DAS GUPTA, Benares.

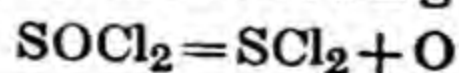
Chlorination, bromination and iodination of monomethyl-*o*-toluidine have been carried out under different conditions as a result of which a number of halogen derivatives of this compound has been obtained.

90. Interaction of thionyl chloride and sulphur dichloride with salicylic acid and its esters.

J. A. KUNDARGI, Y. M. CHAKRADEO, and S. V. SHAH, Kohlapur.

The action of thionyl chloride on ethyl salicylate, methyl salicylate, and phenyl salicylate, and that of sulphur dichloride on the above compounds as well as on salicylic acid, all in the presence of iron dust, zinc dust, and chlorides of iron, zinc, tin, antimony and bismuth, have been investigated.

Products of the type of  $(C_6H_4 \cdot OH \cdot COOR)_2S$  have been formed where R represents  $CH_3$ ,  $C_2H_5$  and  $C_6H_5$ . Thionyl chloride is turned into sulphur dichloride according to the following equation :



and the resulting sulphur dichloride eliminates hydrogen chloride with a hydrogen atom from each of the benzene rings, which are linked to each other through the sulphur atom of sulphur dichloride. The thio-com-



pounds formed are identical with those obtained by Hirve, Jadhav and Chakradeo (*J. Amer. Chem. Soc.*, 1935, 101-103; *Jour. Univ. Bom.*, 1933, 128-31 and *J. Indian Chem. Soc.*, 1934, 551-554).

### 91. Synthetic pungent principles.

P. C. MITTER and SUDHIRCHANDRA RAY, Calcutta.

The naturally occurring pungent principles are found to possess the acylamide (-N-CO-) linking in common, the amine being either primary or secondary. It may be heterocyclic like piperidine as in piperine or fatty-aromatic like vanillylamine as in capsaicin or even purely aliphatic like isobutylamine as in fagaramide. The acid is either aliphatic or fatty-aromatic and contains at least one double bond. The object of this paper was to synthesise a number of isobutylamides, acylated with both saturated and unsaturated acids and to determine the effect of the number of carbon atoms in the chains, the distance of the double bond (if any) from the -N-CO- group, the presence or absence of a phenolic group etc. on pungency.

Altogether the amides of twelve acids have been investigated and some interesting conclusions arrived at.

### 92. The influence of $\alpha$ -phenyl group in three carbon tautomerism.

N. L. PHALANIKAR and K. S. NARGUND, Ahmedabad.

In continuation of previous work (*Proc. Indian Sci. Congress*, 1936, 23) the mobilities and the positions of equilibrium have been determined and are given in the following table.

Compounds.	Catalyst used.	% $\alpha\beta$ at equilibrium.	Mobility.
$\alpha$ -Phenyl cyclohexenyl acetic acid	KOH	42	$0.0095 = 10(K_1 + K_2)$
$\alpha$ -Phenyl cyclohexyldene acetic acid.	KOH	87	$0.50 = 10(K_1 + K_2)$
Phenyl hexenoic acid	C <sub>2</sub> H <sub>5</sub> ONa	72	$0.99 = (K_1 + K_2)10^4$
Ethyl phenylcyclohexylidene acetate		95	$35.6 = (K_1 + K_2)10^4$
Ethyl phenylcyclohexenyl acetate.	C <sub>2</sub> H <sub>5</sub> ONa		
Ethyl phenylhexenoate			
Ethyl phenylhexenoate.			

The results are discussed in relation to the polar behaviour of phenyl group.

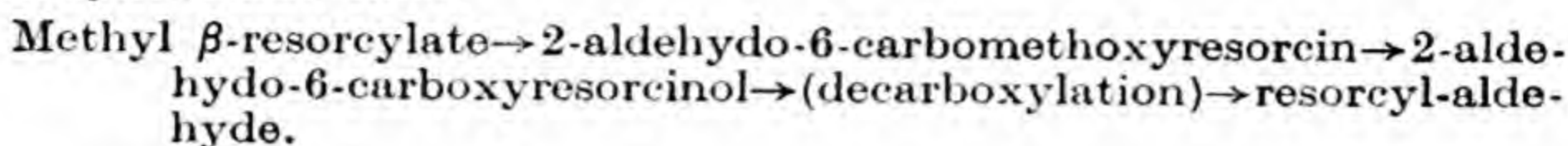
### 93. Synthesis of $\alpha$ -resorcyaldehyde and related compounds.

R. C. SHAH and M. C. LAIWALLA, Bombay.

Methyl  $\beta$ -resorcyate (I) does not undergo the Gattermann reaction under the usual conditions. It is found, however, that under special



conditions, viz. in the presence of anhydrous aluminium chloride dissolved in dry ether (*cf.* Shah, *Current Sci.*, 1934, 157) the reaction proceeds very smoothly and a high yield of the aldehyde-ester (II) is obtained. The aldehydo group is found unexpectedly to enter exclusively the usually inaccessible  $\gamma$ -position in the resorcinol nucleus. This welcome observation has made possible a simple synthesis of  $\gamma$ -resorcyraldehyde, which has been synthesised thus :



The yields are high except during decarboxylation when a 33% yield is obtained.  $\gamma$ -Resorcylic aldehyde has m.p. 155-156°.

$\gamma$ -Resorcyraldehyde has been recently synthesised by a different method (Limaye, *Rasayanam*, 1936, No. 1, Vol. I, Page 13).

The constitution of the aldehyde-ester as methyl 2 : 4-dihydroxy-3-aldehydo-benzoate has been definitely established. The aldehyde ester on reduction gave methyl 2 : 4-dihydroxy-3-methylbenzoate, which on methylation yielded methyl 2-hydroxy-3-methyl-4-methoxybenzoate (of proved constitution) which was found to be identical by direct comparison with the compound prepared by nuclear methylation of  $\beta$ -resorcylic acid by Perkin's method.

A number of related compounds has been prepared from methyl 2 : 4-dihydroxy-3-aldehydo-benzoate including the hitherto unknown 2 : 4-dihydroxy-3-methylbenzoic acid and 2 : 4-dimethoxy-3-methylbenzoic acid.  $\gamma$ -Resorcyraldehyde on reduction gave 2-methyl-resorcinol.

#### 94. Condensation of succinic anhydride with phenolic ethers.

G. A. DALAL and K. S. NARGUND, Ahmedabad.

Succinic anhydride has been condensed with phenolic ethers by Friedel and Crafts' reaction using nitrobenzene as solvent. Resorcinol-dimethyl ether gave  $\gamma$ -keto- $\gamma$ -2 : 4-dimethoxy phenyl butyric acid, m.p. 148°. Hydroquinone dimethylether gave  $\gamma$ -keto- $\gamma$ -2 : 5-dimethoxyphenyl butyric acid, m.p. 107°. Pyrogallol trimethyl ether gave  $\gamma$ -keto- $\gamma$ -2 : 3 : 4-trimethoxyphenyl butyric acid, m.p. 153°. Resorcinol monomethyl ether gave a product which is most likely  $\gamma$ -keto- $\gamma$ -2-hydroxy-4-methoxyphenyl-butyric acid, m.p. 156°.

The constitutions of the above acids have been proved by oxidation. Further work on the condensation of dihydric phenols with succinic anhydride is in progress.

#### 95 Condensation of succinic anhydride with naphthol methyl ethers.

K. P. DAVE and K. S. NARGUND, Ahmedabad.

$\alpha$ -Naphthol methyl ether when condensed with succinic anhydride in nitrobenzene by Friedel and Crafts' method gave  $\gamma$ -keto- $\gamma$ -4-methoxynaphthyl-butyric acid, m.p. 173°. The constitution of this acid has been proved (a) by oxidation to 4-methoxynaphthoic acid, (b) by Clemmensen reduction to 4-methoxy-naphthyl-butyric acid (Kon and Ruzicca, *J.*, 1936, 192), and (c) by synthesis from the Grignard reagent, prepared from 4-bromo- $\alpha$ -naphthol methyl ether and succinic anhydride. The condensation of succinic anhydride with  $\beta$ -naphthol methyl ether confirms the results of Short, Stromberg and Wiles (*J.*, 1936, 320).



## 96. Isomeric triazocinnamic acids.

K. A. NARAIN RAO and P. R. VENKATARAMAN, Annamalainagar.

The isomeric *o*-, *m*- and *p*-triazocinnamic acids have been prepared from the corresponding aminocinnamic acids by diazotization and interaction with sodium azide. They do not explode when heated although they react very violently with concentrated sulphuric acid. The properties of these isomers have been investigated in detail by a study of their behaviour on oxidation, reduction and decomposition involving elimination of nitrogen.

97. Formation and transformation of carbon ring compounds.  
Part IV.

S. C. SENGUPTA, Calcutta.

The present communication deals with the syntheses of hydro-naphthalene derivatives containing a gem-dimethyl substituent and also the effect of selenium dehydrogenation on these compounds. *unsymm*-Dimethyl succinic anhydride condensed with benzene and toluene in presence of aluminium chloride forming  $\beta\beta$ -dimethyl- $\gamma$ -keto- $\gamma$ -phenyl butyric acid (m.p. 170-171°) and  $\beta\beta$ -dimethyl- $\gamma$ -keto- $\gamma$ -(*p*-tolyl)-butyric acid (m.p. 158-159°) respectively. These two keto acids on reduction by the Clemmensen method gave  $\beta\beta$ -dimethyl- $\gamma$ -phenyl butyric acid (m.p. 98°) and  $\beta\beta$ -dimethyl- $\gamma$ -(*p*-tolyl)-butyric acid (m.p. 111-112°), which on cyclization with 85% sulphuric acid gave 1-keto-3 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydro-naphthalene and 1-keto-3 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene respectively. The keto cyclic compounds thus obtained on Clemmensen reduction yielded 3 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydro-naphthalene and 3 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene respectively. These two tetrahydronaphthalene derivatives containing gem-dimethyl substituents on heating with selenium at 300° could not be dehydrogenated to naphthalene or alkyl naphthalenes.

98. Formation and transformation of carbon ring compounds.  
Part V.

S. C. SENGUPTA, Calcutta.

In this paper *unsymm*-dimethyl succinic anhydride has been condensed with naphthalene in presence of anhydrous aluminium chloride giving  $\alpha\alpha$ -dimethyl- $\gamma$ -keto- $\gamma$ -1-naphthyl butyric acid (m.p. 190-91°) and  $\alpha\alpha$ -dimethyl- $\gamma$ -keto- $\gamma$ -2-naphthyl butyric acid (m.p. 170°). These two keto acids on reduction by the Clemmensen method gave  $\alpha\alpha$ -dimethyl- $\gamma$ -1-naphthyl butyric acid (m.p. 99-101°) and  $\alpha\alpha$ -dimethyl- $\gamma$ -2-naphthyl butyric acid (m.p. 133-135°) which on cyclization with 85% sulphuric acid gave 1-keto-2 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (m.p. 68-69°) and 4-keto-3 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (b.p. 185-187°/8 mm.) respectively. Clemmensen reduction of these two keto-phenanthrene derivatives gave 2 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene and 3 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene. On selenium dehydrogenation at 340° the former gave 2-methyl phenanthrene but the latter gave an inseparable mixture which seemed to contain phenanthrene and methyl-phenanthrene.

99. Formation and transformation of carbon ring compounds.  
Part VI.

S. C. SENGUPTA, Calcutta.

$\alpha$ -Methylnaphthalene and *unsymm*-dimethyl succinic anhydride condensed in presence of aluminium chloride giving  $\alpha\alpha$ -dimethyl- $\gamma$ -



keto- $\gamma$ -(4-methyl)-1-naphthyl-butyric acid (m.p. 202-203°), which on Clemmensen reduction gave  $\alpha\alpha$ -dimethyl- $\gamma$ -(4-methyl)-1-naphthyl butyric acid (m.p. 105-106°). The latter on cyclization with 85% sulphuric acid gave 1-keto-2 : 2 : 9-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (m.p. 123°) in almost theoretical yield. This cyclic keto compound on Clemmensen reduction gave 2 : 2 : 9-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (m.p. 90-91°) which on selenium dehydrogenation at 340° gave 2 : 9-dimethylphenanthrene, melting at 55-56°.

#### 100. A synthesis of chrysene.

S. C. SENGUPTA, Calcutta.

By an extension of the method developed for the synthesis of spirohydrocarbons and their ring transformation (*J. Indian Chem. Soc.*, 1934, 389), the following synthesis of chrysene has been accomplished. The anhydride of cyclopentane-1-carboxy-1-acetic acid reacted with naphthalene in presence of anhydrous aluminium chloride with the formation of  $\alpha\alpha$ -cyclopentane- $\beta$ -1-naphthoyl-propionic acid (m.p. 140-141°) and  $\alpha\alpha$ -cyclopentane- $\beta$ -2-naphthoyl-propionic acid (m.p. 190-191°). The former on reduction by the Clemmensen method gave  $\alpha\alpha$ -cyclopentane- $\beta$ -1-naphthyl butyric acid whence was prepared 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene-2 : 2-spirocyclopentane (b.p. 215°/6 mm.). This spiro-ketone was reduced by the Clemmensen method to the spirohydrocarbon 1 : 2 : 3 : 4-tetrahydrophenanthrene-2 : 2-spiro-cyclopentane, which on selenium dehydrogenation at 300-350° gave only chrysene and no trace of benzanthracene could be detected in the product.

#### 101. Synthesis in the phenanthrene series.

S. S. AHUJA, K. S. NARANG, and J. N. RAY, Lahore.

6-Nitro-3 : 4-dimethoxybenzylidene benzyl cyanide (m.p. 179°) gives 6-amino-3 : 4-dimethoxybenzylidene benzyl cyanide (m.p. 154°) on reduction but the Pschorr synthesis on the latter did not succeed. Piperonylidene benzyl cyanide (m.p. 119°) nitrates to give 6-nitro-3 : 4-methylenedioxy benzylidene-cyanostilbene (m.p. 212°) which reduces to the amino compound (m.p. 177°); the Pschorr synthesis when applied to this compound also fails. 3 : 4-Dimethoxy-6-nitro-benzyl alcohol (m.p. 129°) prepared by Cannizzaro reaction on 6-nitroveratric aldehyde gives an acetyl derivative (m.p. 162°) and is converted easily to 6-nitro-3 : 4-dimethoxybenzyl chloride (m.p. 92°). The reaction of the latter with potassium cyanide gives two polymers, m.p. 167° and 234° respectively. Dimethoxybenzyl cyanide (m.p. 51°) nitrates to give 6-nitro-3 : 4-dimethoxybenzyl cyanide (m.p. 113°). This substance condenses with piperonal to give piperonylidene-6-nitro-3 : 4-dimethoxybenzyl cyanide (m.p. 198°). On reduction, this compound gave a substance in which amino group was absent.

6-Bromo-3 : 4-dimethoxybenzyl cyanide (m.p. 89°) condenses with 6-bromopiperonal to give cyano-3 : 4-dimethoxy-6-bromo-3' : 4'-methylenedioxy-6'-bromostilbene. The action of copper on this compound is being tried.

#### 102. Chalkones : 2-Methoxy styryl phenyl ketone.

N. A. BHAGVAT and T. S. WHEELER, Bombay.

The dibromide (II) of 2-methoxy-styryl-phenyl-ketone (I) when boiled with methyl alcohol and ethyl alcohol gives respectively  $\alpha$ -benzoyl- $\alpha$ -bromo- $\beta$ -2-methoxy phenyl- $\beta$ -methoxy ethane (III) and  $\alpha$ -benzoyl- $\alpha$ -bromo- $\beta$ -2-methoxy phenyl- $\beta$ -ethoxy ethane (IV). The action of pyridine on (I) leads to the unsaturated bromo ketone,  $\alpha$ -benzoyl- $\alpha$ -bromo- $\beta$ -2-methoxy-phenyl-ethylene (V). The action of chlorine on



(I) gives the dichloride, which in boiling methyl and ethyl alcoholic solutions is converted into the  $\beta$ -alkyloxy compounds analogous to (III) and (IV). Pyridine likewise converts the dichloride into the unsaturated chloroketone. (I) with bromine (2 mols) gives  $\alpha$ -benzoyl- $\beta$ -2-methoxy-5-bromophenyl- $\alpha$ - $\beta$ -dibromo-ethane (VI). The  $\beta$ -bromine atom in (VI) is also reactive; it can be replaced by a methoxy or ethoxy group by the action of boiling methyl or ethyl alcohol, and can be eliminated as hydrogen bromide by pyridine, giving  $\alpha$ -benzoyl- $\alpha$ -bromo- $\beta$ -2-methoxy-5-bromophenyl-ethylene.

103. Chalkones and chalkone oxides. 2 : 4-Dimethoxyphenyl-3' : 4'-methylenedioxystryl ketone.

D. C. MOTWANI and T. S. WHEELER, Bombay.

In the present work the authors propose to study the effect of methoxy groups, in the ketone nucleus of the chalkone, on the reactivity of the bromine atoms of the chalkone dibromide. For this purpose 2 : 4-dimethoxyphenyl-3' : 4'-methylenedioxystryl ketone, m.p. 137-138°, has been prepared: (i) from 2 : 4-dimethoxyresacetophenone and piperonal, and (ii) from piperonal and resacetophenone and subsequent methylation of the resulting product. The chalkone has been prepared before by Goschke and Tambor (*Ber.*, 1911, 3504) by method (ii) who, however, give the m.p. as 168°. The dibromide of the chalkone is prepared from its solution in a mixture of carbon bisulphide and chloroform by the action of bromine. One of the bromine atoms shows the usual reactivity. Potassium iodide regenerates the chalkone from a solution of the dibromide in acetone solution. The oxide of the chalkone has been prepared by the action of alkaline hydrogen peroxide. Its derivatives have been prepared.

Further work is in progress.

104. Reactivity of *p*-Anisylidene-*p*-methylacetophenone.

S. M. NADKARNI and T. S. WHEELER, Bombay.

In continuation of the work on *p*-anisylidene-*p*-methylacetophenone (I) communicated last year, the dibromide, (II) of *p*-tolyl-4-methoxystyryl ketone (I) and the dibromide of *p*-tolyl-4-methoxy-3-bromo-styryl ketone (III) give with two molecules of sodium methoxide followed by hydrolysis, *p*-tolyl-4-methoxyphenyl diketone and a corresponding bromo-diketone which with copper acetate give green copper salts. (III) condenses with ethyl acetoacetate to yield ethyl 2-(4'-methoxy-3-bromophenyl)-4-toluoyl- $\Delta^4$ -cyclohexene-6-one-1-carboxylate (IV). This with hydrochloric acid under pressure gives 4'-methoxy-3-bromo-phenyl-4-toluoyl- $\Delta^4$ -cyclohexenone (V).

The dichloride (VI) of (I) behaves in the same way as the dibromide mentioned before with regard to methyl and ethyl alcohol, pyridine, sodium methoxide (one mol), potassium iodide, etc. The same reactions are observed with the dichloride (VII) of *p*-tolyl-4-methoxy-3-chlorostyryl ketone (VIII). (VII) is obtained by the action of excess of chlorine on (I), and with two molecules of sodium methoxide followed by hydrolysis gives a chlorodiketone (IX) which with copper acetate gives a green chloro copper salt. (VIII) condenses with acetoacetic ester to give a chloro-ester and thence a chloro- $\Delta^4$ -cyclohexenone corresponding to (IV) and (V).

(VIII) with bromine or the dibromide of (I) with chlorine gives a chlorodibromide (X) which with methyl and ethyl alcohol gives a chloromethoxy bromide and a chloro-ethoxy bromide respectively. (X) with pyridine or sodium methoxide (one mol) yields  $\alpha$ -toluoyl- $\alpha$ -bromo- $\beta$ -4-methoxy-3-chlorophenylethylene. Similarly *p*-tolyl-4-methoxy-3-bromostyryl ketone gives with chlorine a bromodichloride (XI). (VI) with



bromine gives the same compound. (XI) gives with methyl and ethyl alcohols a bromo-methoxy chloride and a bromo-ethoxy chloride respectively. (XI) yields with pyridine or sodium methoxide (one mol)  $\alpha$ -toluoyl- $\alpha$ -chloro- $\beta$ -4-methoxy-3-bromophenyl-ethylene. The alkoxy chlorides give with HBr  $\alpha$ -*p*-toluoyl- $\alpha$ -chloro- $\beta$ :4-methoxyphenyl-bromethanes.

### 105. Reactivity of piperonylidene-*p*-methylacetophenone.

A. M. WARRIER and T. S. WHEELER, Bombay.

Extending the work on the reactivity of piperonylidene-*p*-methylacetophenone communicated last year, hydrolysis of the nitriles has been carried out. The action of two mols of sodium alkoxides on the dibromides of *p*-tolyl-3:4-methylene-dioxystyryl ketone (I) and *p*-tolyl-3:4-methylenedioxy-6-bromostyryl ketone (II) has been found to give ethers which with hydrochloric acid yield  $\beta$ -diketones. These diketones coloured ferric chloride (alcoholic) green and with copper acetate yielded the corresponding copper salts. *p*-Tolyl-3:4-methylenedioxy-styryl ketone (III) and *p*-tolyl-3:4-methylenedioxy-6-bromo-styryl ketone condensed with ethyl acetoacetate to give ethyl 2-(3':4'-methylenedioxy-phenyl)-4-toluoyl- $\Delta^4$ -cyclohexene-6-one-1-carboxylate (IV) and ethyl 2-(3':4'-methylene-dioxy-6-bromo-phenyl)-4-toluoyl- $\Delta^4$ -cyclohexene-6-one-1-carboxylate (V) respectively. (IV) and (V) on hydrolysis with hydrochloric acid under pressure yielded the respective cyclohexenones. Chlorination of the parent substance was also carried out and compounds corresponding to the bromo compounds have been obtained. Several mixed halogeno compounds, with different kinds of halogen atoms, in the nucleus and in the side chain, as well as in the side chain only, have also been prepared.

### 106. Studies in Pechmann's and Simonis' reactions.

D. CHAKRAVARTI and B. BANERJEE, Calcutta.

4-Chloro-*o*-cresol, 4-nitro-*o*-cresol, 2-chloro-*p*-cresol, 4-chloro-*m*-cresol and 2-nitro-*m*-cresol have been condensed with various  $\alpha$ -alkyl-acetoacetic esters using sulphuric acid (Pechmann's reaction) and phosphorus pentoxide (Simonis' reaction) as condensing agents.

4-Chloro-*o*-cresol, 4-nitro-*o*-cresol and 2-nitro-*m*-cresol do not react with the esters in presence of sulphuric acid but in presence of phosphorus pentoxide chromones are obtained.

2-Chloro-*p*-cresol and 4-chloro-*m*-cresol form coumarins with sulphuric acid but chromones with phosphorus pentoxide. The coumarin formation is hindered with the introduction of heavier alkyl substituents in the acetoacetic ester molecule. The chromones have all been characterized by the formation of styryl derivatives.

It is found that Simonis' reaction on the formation of chromones can be facilitated by introducing halogen and nitro groups into the molecules of the phenols which do not satisfactorily respond to Pechmann's reaction.

### 107. Synthesis of 4-methyl-6-acetyl-8-ethyl-7-hydroxycoumarin.

(MISS) INDU GHATE, Poona.

(Communicated by D. B. Limaye.)

In continuation of the work of Limaye and Ghate (*Rasayanam*, 1936, 1, 39), 2-ethyl-resorcin has been condensed with ethyl acetoacetate. The resulting 4-methyl-8-ethyl-7-hydroxycoumarin,  $C_{12}H_{12}O_3$ , m.p.  $226^\circ$ , gave an acetate,  $C_{14}H_{14}O_4$ , m.p.  $105^\circ$ , which on aluminium chloride treatment yielded 4-methyl-6-acetyl-8-ethyl-7-hydroxycoumarin,  $C_{14}H_{14}O_4$ , m.p.  $166^\circ$ , characterized by its acetate  $C_{16}H_{16}O_5$ , m.p.  $104^\circ$  and the



hydrolytic product, 2:4-dihydroxy-3-ethyl- $\beta$ -methylcinnamic acid,  $C_{14}H_{16}O_5$ , m.p. 131–133° (with evolution of carbon dioxide). It forms a phenolic product, m.p. 68°–70°, when heated at its m.p.

The 4-methyl-6-acetyl-8-ethyl-7-hydroxycoumarin, m.p. 166°, is being used for obtaining a condensed ring system such as a furo-coumarin having an alkyl group in the 8-position.

#### 108. On the limited applicability of Kostanecki's reaction.

D. CHAKRAVARTI and P. BAGCHI, Calcutta.

4-Chloro-2-aceto-1-naphthol (m.p. 121°, phenylhydrazone, m.p. 158–159°), and 4-chloro-2-propio-1-naphthol (m.p. 88°), prepared respectively from the acetyl or propionyl derivative of 4-chloro-1-naphthol (Fries' rearrangement), have been submitted to Kostanecki's reaction. When heated with sodium acetate and acetic anhydride, these ketonaphthols form chromones: 4-chloro-2-aceto-1-naphthol gives 6-chloro-2-methyl-3-acetyl-1:4- $\alpha\beta$ -naphthapyrone (m.p. 188–89°), 4-chloro-2-propio-1-naphthol gives 6-chloro-2:3-dimethyl-1:4- $\alpha\beta$ -naphthapyrone (m.p. 182–83°), identical with the condensation product of 4-chloro-1-naphthol with ethyl methylacetoacetate in presence of phosphorus pentoxide (*Proc. Ind. Sci. Cong.*, 1936). With sodium propionate and propionic anhydride they yield coumarins, the coumarin from 4-chloro-2-aceto-1-naphthol being identical with the product obtained by condensing 4-chloro-1-naphthol with ethyl methylacetoacetate using sulphuric acid as the condensing agent. Using phenyl acetic anhydride and sodium phenyl acetate, 4-chloro-2-aceto-1-naphthol yields a coumarin e.g. 6-chloro-4-methyl-3-phenyl-1:2- $\alpha\beta$ -naphthapyrone (m.p. 215°) identical with the condensation product of 4-chloro-1-naphthol with ethyl phenyl acetoacetate in presence of sulphuric acid.

The results obtained are in agreement with the observations of Heilbron and co-workers (*J.*, 1933, 1263; 1934, 1311, 1581; 1936, 295).

#### 109. Coumarin-carboxylic acids.

R. C. SHAH and S. M. SETHNA, Bombay.

Clayton (*J.*, 1908, 2016) showed that the carboxyl and the carbethoxyl groups in phenol inhibit Pechmann's coumarin condensation. It is now found that  $\beta$ -resorcylic acid, methyl  $\beta$ -resorcylate and *p*-orsellinic acid undergo the coumarin condensation readily with acetoacetic ester and malic acid giving the corresponding coumarin carboxylic acid derivatives. The constitutions of the coumarins have been established. Further work is in progress.

#### 110. Synthesis of coumarins and chromones from 4-bromo-1-naphthol and alkyl-acetoacetic esters.

D. CHAKRAVARTI and P. BAGCHI, Calcutta.

4-Bromo-1-naphthol (Reverdin and Kaufmann, *Ber.*, 1895, 28, 3049) condenses with ethyl acetoacetate forming a coumarin, e.g. 6-bromo-4-methyl-1:2- $\alpha\beta$ -naphthapyrone, m.p. 208°, with sulphuric acid or phosphorus pentoxide as condensing agent. With the introduction of an alkyl substituent in the acetoacetic ester molecule, however, as with ethyl methyl-acetoacetate 4-bromo-1-naphthol yields a coumarin, e.g. 6-bromo-3:4-dimethyl-1:2- $\alpha\beta$ -naphthapyrone, m.p. 188°, with sulphuric acid and a chromone (6-bromo-2:3-dimethyl-1:4- $\alpha\beta$ -naphthapyrone, m.p. 211–12°) with phosphorus pentoxide. The 1:4-naphthapyrone is characterized by the formation of the styryl derivative, m.p. 233°.



111. Synthesis of coumarins from phenol-carboxylic acids and  $\beta$ -ketonic esters.

D. CHAKRAVARTI and B. BANERJEE, Calcutta.

Clayton (*J.*, 1908, 2018) showed that nitrophenols and phenol-carboxylic acids do not respond to Pechmann's reaction and the halogenated phenols form coumarins in very poor yield. In continuation of the work of Chakravarti and Ghosh (*J. Indian Chem. Soc.*, 1935, 12, 622; *Proc. Ind. Sci. Cong.*, 1935, 153) it has been found that the presence of a carboxyl group in those phenols which readily form coumarins does not inhibit the reaction. 7-Hydroxy-4-methyl-coumarin-6-carboxylic acid (m.p.  $282^{\circ}$ ) is formed by condensing  $\beta$ -resorcylic acid with ethyl acetoacetate. The work on the condensation of other phenolic acids is in progress.

112. On the constitution of nitro- $\beta$ -methyl-umbelliferone methyl ether and chloro-resorcin.

D. CHAKRAVARTI and B. BANERJEE, Calcutta.

The nitro- $\beta$ -methyl-umbelliferone methyl ether (m.p.  $281^{\circ}$ ) of Pechmann and Obermiller (*Ber.*, 1901, 34, 666) has been shown to be 6-nitro-7-methoxy-4-methylcoumarin since on demethylation it gives 6-nitro-7-hydroxy-4-methylcoumarin (m.p.  $255^{\circ}$ ), identical with the coumarin obtained by condensing 4-nitroresorcin with ethyl acetoacetate.

6-Chloro-7-methoxy-4-methyl-coumarin (m.p.  $252^{\circ}$ ), obtained by Sandmeyer's reaction on 6-amino-7-methoxy-4-methylcoumarin (m.p.  $120^{\circ}$ ), the reduction product of 6-nitro-7-methoxy-4-methyl-coumarin, is identical with the methoxy derivative of the coumarin obtained by the condensation of chloro-resorcin and ethyl acetoacetate. The chlorine atom in chlororesorcin, therefore, occupies the position 4 as shown by Clark (*J. Amer. Chem. Soc.*, 1933, 319) and Chakravarti and Ghosh (*J. Indian Chem. Soc.*, 1935, 12, 791; *Proc. Ind. Sci. Cong.*, 1935, 152).

## 113. Use of 7-hydroxycoumarin in the Nidhone process for the syntheses of 2-acyl-resorcins and the preparation of 3-methyl-furocoumarins.

M. C. JOSHI, Poona.

(Communicated by D. B. Limaye.)

In continuation of Limaye's work on the syntheses of furocoumarins (linear and angular) and the Nidhone process (*Ber.*, 1932, 65, 375; 1934, 67, 12; Limaye and Gangal, *Rasayanam*, 1936, 1, 15) the acetate of 7-hydroxycoumarin was treated with aluminium chloride when two isomeric acetyl umbelliferones were isolated, as in the case of 4-methyl-umbelliferone. The substance, m.p.  $167^{\circ}$ , which formed the major part of the reaction, was previously obtained by Limaye, and has been described by Ray, Silooja and Vaid (*J.*, 1935, 813) as the 8-acetyl-7-hydroxycoumarin. On hydrolysis with caustic alkali, it gave an acid of indefinite melting point, together with a small quantity of 2-acetyl-resorcin (Limaye and Gangal, *Proc. Ind. Sci. Cong.*, 1934, 229) confirming the structure of the substance as the 8-acetyl compound. The other substance, m.p.  $177^{\circ}$ , does not give 2-acetyl-resorcin on hydrolysis and hence it is the 6-acetyl-7-hydroxycoumarin.

The 8-acetyl-7-hydroxy-coumarin was successively converted into the 7-(carbethoxy-methoxy)-8-acetyl-coumarin, m.p.  $117^{\circ}$ , the 7-(carboxy-methoxy)-8-acetylcoumarin, m.p.  $210-212^{\circ}$  and the angular 3-methyl-7':8'-furocoumarin, m.p.  $150^{\circ}$ . The 6-acetyl-7-hydroxycoumarin when similarly treated gave the linear 3-methyl-7':6' furocoumarin, m.p.



188°. A furocoumarin of the same structure and m.p. has been described by Ray, Silooja and Vaid (*loc. cit.*) who obtained it by condensing 7-hydroxycoumarin with chloroacetone.

#### 114. Chalkones and flavones from 2-acetyl-resorcinol.

I. Z. SAIYED and T. S. WHEELER, Bombay.

It has been shown in the previous communication (*Proc. Ind. Sci. Cong.*, 1936) that 2-acetyl-resorcinol when condensed with various aldehydes in presence of alkali gave a mixture of chalkones and flavanones. Attempts to separate the two from their mixture were unsuccessful. With benzaldehyde, however, the flavanone (m.p. 302-303°) has been isolated.

The dimethyl ether of 2-acetyl-resorcinol has been condensed with benzaldehyde, salicylaldehyde, anisaldehyde, *o*-nitrobenzaldehyde, piperonal and *o*-chlorobenzaldehyde in presence of alkali. In all the cases chalkones have been readily obtained. The di- and tri-bromides of these chalkones and their reactions are being studied.

8-Acetyl- $\beta$ -methyl-umbelliferone has also been condensed with anisaldehyde, *o*-chloro-benzaldehyde and *o*-nitrobenzaldehyde in presence of alkali and their corresponding compounds have been obtained with some difficulty.

4-Methoxy-5-hydroxy-flavone (m.p. 155°) has been obtained by Robinson's method from 2-acetyl-resorcinol, anisic anhydride, and sodium anisate. Its demethylation has led to 4':5-dihydroxyflavone (m.p. 239-40°). The synthesis of the corresponding 5-hydroxyflavones from 3:4-dimethoxybenzoic acid, *o*-methoxy-benzoic acid, *m*-methoxybenzoic acid, 3:4-methylenedioxybenzoic acid and dimethyl- $\beta$ -resorcylic acid, is in progress.

The dibenzoate (m.p. 106-7°) of 2-acetyl-resorcinol in presence of sodamide in ether, is converted into the diketone, which with concentrated sulphuric acid gives 5-hydroxyflavone.

From 2-acetyl-resorcinol, *o*-methoxy-dibenzoate, 3:4-methylenedioxybenzoate and dianisate have been prepared and the sodamide reaction on them is being studied.

#### 115. Di-flavones and di-flavonols.

D. R. NADKARNI and T. S. WHEELER, Bombay.

The di-ether (*J.*, 1936, 589) obtained in the condensation of epichlorohydrin or glyceryl chlorohydrin with resacetophenone has been treated with aldehydes to give several di-chalkones which have been converted into di-flavones and di-flavonols with selenium dioxide and 30% hydrogen peroxide, respectively.

#### 116. The constitution of a colouring matter of *Digitalis lutea*.

H. S. MAHAL and K. VENKATARAMAN, Bombay.

The flavone colouring matter of *Digitalis lutea* (Adrian and Trillat, 1899) is not identical with 7-methoxy-4'-hydroxy-flavone ('*epipratol*'). The latter has been synthesized by the oxidation of 2-hydroxy-4-methoxy-phenyl-4-benzyloxystyryl ketone with selenium dioxide, followed by debenzoylation.

#### 117. Synthetical experiments in the isoflavone group.

P. C. JOSHI and K. VENKATARAMAN, Lahore.

The action of trichloroacetic anhydride and potassium trichloroacetate on 2-phenylacetyl-1-naphthol gave a substance, which had the qualitative properties of 2-trichloromethyl-3-phenyl-1:4-naphthapyrone, but it could



not be crystallized and hydrolysis to the 2-carboxylic acid and decarboxylation to the naphthaisoflavone were not accomplished.

2 : 4-Dinitrobromobenzene condensed with  $\alpha$ -formylphenyl-acetonitrile in pyridine solution to give 2 : 4-dinitrophenoxy-methylene benzyl cyanide. Saturation of an ethereal solution of the latter with hydrogen chloride gave a substance which was not the dinitroisoflavone, nor was it the pyrone-imide, being unaffected by boiling concentrated hydrochloric acid and syrupy phosphoric acid. Similarly the dinitrophenoxy-methylene phenyl-acetic ester was prepared ; attempts to effect ring closure to the isoflavone were unsuccessful.

Condensing 2 : 4-dinitrobromobenzene with benzoylacetonitrile in presence of sodium ethylate, two substances, the *O*-phenyl and the *C*-phenyl derivatives were isolated. Treatment of the former with hydrogen chloride in ether yielded uncrystallizable material or the original compound.

In the Baker-Robinson method for the synthesis of isoflavones by the oxidation of 2-styryl derivatives the possibility of the use of the dinitrostyryl compound leading to more facile oxidation could not be examined, since 2 : 4-dinitrobenzaldehyde did not condense with 2-methyl-3-phenyl-1 : 4- $\alpha$ -naphthapyrone, which reacts readily with benzaldehyde, anisaldehyde and veratraldehyde.

$\beta$ -Naphthol condenses with ethyl acetoacetate to give a chromone (Dey and Lakshminarayanan, *J. Indian Chem. Soc.*, 1932), but the  $\alpha$ -pyrone was obtained in the case of  $\alpha$ -formylphenylacetic ester.

118. The isolation of an anthocyanin pigment from the rind of sugar cane (*Purple Mauritius*).

C. J. DASARAO, D. G. WALAWALKAR, and B. S. SRIKANTAN, Waltair.

The anthocyanin pigment occurring on the rind of the *purple mauritius* cane has been isolated and identified to be a diglucoside of the monomethyl-ether of delphinidin, possibly ampelopsidin. It has an absorption band at 4400–4800  $\text{\AA}$ .

119. Synthetical experiments on 5 : 8-dihydroxyflavone and on 5 : 6 : 7- and 5 : 7 : 8-trihydroxyflavones.

G. K. BHARADWAJ and K. VENKATARAMAN, Lahore.

The oxidation of chrysin by means of chromic anhydride and with other oxidising agents (nitric acid, potassium persulphate, selenium dioxide) has not led to any homogeneous material other than the starting substance. Oxidation of 5-hydroxy-6-benzyl-7-benzyloxyflavone also gave negative results. The ready oxidisability of pyrogallol trimethyl ether to 2 : 6-dimethoxyquinone suggested that the oxidation of 7 : 8-dihydroxyflavone may lead to norwogonin. Numerous attempts, however, to oxidise 7 : 8-dihydroxyflavone, its dibenzyl ether and dimethyl ether were fruitless. If the dibenzyl ether had been successfully oxidised to the quinone a route to wogonin would have become available.

The persulphate oxidation of 7 : 8-dibenzyloxy coumarin with the object of preparing the 6-hydroxy derivative, which could then be converted through obvious steps to fraxetin, did not proceed as desired, daphnetin being recovered in some cases and the odour of benzaldehyde, indicating debenzylation and oxidation of the benzyl chloride, noticed in others.

An attempted synthesis of baicalein through 2 : 6-dimethoxy-3-acetylbenzoquinone and 2 : 4-dimethoxy-3 : 6-dihydroxyacetophenone broke down at the first stage of the oxidation of gallacetophenone trimethyl ether by means of nitric acid.



The synthesis of wogonin is in progress, involving the partial demethylation of 5 : 8-dimethoxy-7-hydroxyflavone, prepared by the selenium dioxide oxidation of the chalcone derived from 2 : 4-dihydroxy-3 : 6-dimethoxyacetophenone.

With regard to methods for the synthesis of the colouring matter of *gingko biloba* and the synthesis of primetin, the coupling of 8- and 6-hydroxyflavone with diazobenzene chloride and with slow-coupling diazo salts is being studied.

## 120. The constitution of gardenin.

P. K. BOSE and R. NATH, Calcutta.

Gardenin of Stenhouse and Groves (*Annalen*, 1880, 200, 311) is a derivative of heptahydroxyflavone. It contains six methoxy and one hydroxy groups. The latter is present in the benzopyrone nucleus but not in position 3. Three methoxy groups occupy 3' : 4' : 5'-positions. Acetyl and methyl-gardenin are described. 'Gardenic acid' is a quinone formed by loss of a methyl group. The several possibilities are discussed.

## 121. On the exudation from *Celtis cinnamomea* Lind. Isolation of skatol.

P. R. KRISHNASWAMY and B. L. MANJUNATH, Bangalore.

The finely powdered product, on steam distillation, yielded pure skatol (35 per cent.). It is of interest to note that skatol occurs in *Celtis reticulosa* Mig, and *Celtis durandii* Engl. (cf. Wehmer, 'Die Pflanzenstoffe', 1929, II, 235).

## 122. The action of selenium oxychloride on diaryl secondary amines.

K. S. VENKAT RAMAN and P. S. VARMA, Benares.

The selenium analogue of diphenylthiazine and its derivatives have been prepared by heating diarylamines with selenium dichloride in benzene solution (Weizmann and Stephen, 1913, Wilhelm and Cornelius, *J. pr. Chem.*, 1913, ii, 88, 395-408). As selenium oxychloride gave rise to selenides but not selenoxides with tertiary amines, it was expected that with diaryl-amines, it may give diphenyl thiazine derivatives. But the products obtained from (1) diphenylamine, and (2) phenyl  $\alpha$ -naphthylamine are highly coloured, difficultly soluble in the common organic solvents, but soluble in pyridine and amines and contain chlorine. Probable structures of the compounds have been advanced.

The selenium compound so obtained from diphenylamine on nitration with concentrated nitric acid, gives a nitro derivative, soluble in alcohol, and dissolves in aqueous alkali yielding strawberry red solution. The action of selenium oxychloride on other diaryl amines is under investigation. Attempts are being made to prepare selenazine derivatives by the action of selenium on diarylamines, in presence of anhydrous aluminium chloride on the lines similar to the preparations of the corresponding thiazine compounds (Bernthsen, *Ber.*, 1883, 16, 2897; *Annalen*, 1885, 230, 77).

## 123. The action of selenium oxychloride on tertiary amines.

K. S. VENKAT RAMAN and P. S. VARMA, Benares.

Whereas the action of selenium oxychloride on phenols has been thoroughly studied (Michaelis and Kunckell, *Ber.*, 1895, 28, 609; 1897, 30, 2823; Morgan and Burstall, *J.*, 1928, 130, 3260) the reaction with amines has not been so well investigated. It has been reported that



selenium oxychloride reacts with dimethyl and diethyl anilines to give rise to tetra alkyl diamino-diphenyl selenide (Godchaux, *Ber.*, 24, 765). On repeating the experiment it was found that the yield of the compound was poor. The isolation of the compound was found to be rather tedious and there was much loss of material. By changing the conditions of the experiment it has been possible to prepare and isolate the compounds in comparatively good yields in a purer condition. With selenium oxychloride, methyl benzyl aniline gives di- (methyl benzyl-amino phenyl) selenide, m.p. 116°. The reaction with primary amines and other secondary amines is under investigation.

#### 124. Constitution of Guareschi's pyridine derivative.

NIRMALANANDA PALIT, Patna.

Guareschi's compound, m.p. 222-223° (*Chem. Zentr.*, 1897, 927; 1907, I, 332) which has been obtained by revised method from benzyldene-acetoacetic ester and cyanoacetamide with diethylamine as the condensing agent (*Proc. Ind. Sci. Cong.*, 1936) is now shown to be 2-ethoxy-2-hydroxy-3-aceto-4-phenyl-5-cyano-6-keto-hexahydropyridine (I).

Its constitution is based on (a) the formation of a dimethoxy derivative (II), (b) its transformation with acetic anhydride into 2-keto-3-aceto-4-phenyl-6-ketopiperidine (III), (c) with phosphorus trichloride in hot benzene into 2-keto-3-aceto-4-phenyl-5-cyano-6-ketopiperidine (IV), and (d) by the analogy with the condensation product obtained from benzyldene-cyanacetic ester and cyanoacetamide with diethylamine as the condensing agent which is 2-diethylamino-2-hydroxy-3-cyano-6-phenyl-5-cyano-6-ketopiperidine (V).

That (V) is not an open chain derivative but a ring compound is proved by its ready transformation into 2-keto-3-cyano-4-phenyl-5-cyano-6-oxyquinoline (VI) which has been previously obtained by Day and Thorpe (*J.*, 1920, 1473) by a different method and whose constitution has been established.

#### 125. Quinoline derivatives. Part I.

T. N. GHOSH, Bangalore.

Antipyrine has greater antipyretic activity than quinine, but has no specific action against malaria. It was, therefore, thought that quinoline derivative with fused pyrazolone ring will have antipyretic activity combined with antimalarial properties. 1-Phenyl-3-methyl-pyrazolone has now been condensed with anthranilic acid to yield a pyrazolinoquinoline derivative.

The condensation of hippuric acid with anthranilic acid, in presence of fused sodium acetate, has been studied.

Urethanylacetic ester has been condensed with *o*-nitrobenzaldehyde to yield  $\alpha$ -urethanyl-*o*-nitrocinnamic ester. Attempts are being made to reduce this nitro compound with various reducing agents.

#### 126. Quinoline derivatives. Part II.

T. N. GHOSH, Bangalore.

Therapeutic activity of thiazole and benzthiazole derivatives is well known. It was, therefore, thought that thiazole quinoline derivatives will possess important therapeutic properties.

When treated with acetic anhydride, thiocarbamidoacetic acid is easily converted into a thiazole derivative which, due to the presence of a reactive methylene group, readily condenses with *o*-nitrobenzaldehyde, the product yielding a thiazolequinoline derivative on reduction.



## 127. Indigoid vat dyes of the isatin series. Part II.

S. K. GUHA, Patna.

The present investigation was undertaken with the object of preparing 3-indole-2'-(6'-methyl)-thionaphthene-indigos and comparing them with those of the corresponding 5-methyl compounds (Guha and Basu-Mallick, *J. Indian Chem. Soc.*, 1934, 11, 395). It was intended to examine how far Martinet's rule (*Rev. Gen. Mat. Col.* 1921, 25, 17) is obeyed by 3-indole-2'-thionaphthene-indigo commercially known as Thioindigo Scarlet R (Bezdzik and Friedlander, *Monatsh.*, 1908, 29, 376; E.P. 17162-06; D.R.P. 241327) and its derivatives (Ciba red G.E.P. 19158-07; G.P. 277358) having one methyl group present in the thionaphthene nucleus of the molecule. Isatin and its various substitution products and also phenanthraquinone were condensed with 6-methyl-3-hydroxy-thionaphthene and the corresponding indigoid dyes obtained. Their properties have been investigated.

## 128. Synthesis of arsindole derivatives.

H. N. DAS GUPTA, Calcutta.

The action between phenyl acetylene and phenyl arsenious chloride has been studied and it has been found possible to isolate an addition product in which Cl and PhAsCl serve as addenda to the triple bond.

The above compound when subjected to Friedel and Crafts' reaction leads to the production of 1-phenyl-3-chloro-arsindole (arsindole=indole in which NH is replaced by AsH).

129. Investigations of the constitution of 'artostenone', a keto-compound related to sterols, present in an Indian summer fruit '*Artocarpus integrifolia*'. Part I. Isolation and purification of artostenone.

M. C. NATH, Dacca.

1. Artostenone, a solid ketone, isolated from the fruit of *Artocarpus integrifolius* has the composition  $C_{30}H_{50}O$ , m.p. 109°.

2. It is highly soluble in most of the organic solvents.

3. Its specific rotation is  $[\alpha]_D^{29} = 19.86$  in absolute alcohol

and  $[\alpha]_D^{29} = 23.44$  in chloroform.

4. The molecular weight as determined by cryoscopic method is 407.3, that from X-ray data is 418 and the molecular elementary composition, as obtained by combustion results, suggests the molecular weight to be 426.

5. The density of artostenone, as found by suspension method, is 1.08.

6. It gives a monoxime, m.p. 175° and semicarbazone, m.p. 202-3°.

7. It gives some of the colour reactions of sterols, Kahlenberg's reaction which is specific for ergosterol being most pronounced.

8. Artostenone is an unsaturated compound.

## 130. Investigations on the constitution of 'artostenone'. Part II. Double bond in artostenone.

M. C. NATH, Dacca.

1. Artostenone is an unsaturated compound with only one double bond.

2. Number of bromine atoms which enter a molecule of artostenone, on bromination in carbon tetrachloride solution is four.



3. Two bromine atoms enter the molecule by substitution and the remaining two by addition.

4. The tetrabromo compound has been isolated and the percentage of bromine has been found to be 43.4 (Piria and Schiff's method).

5. Iodine value of artostenone has been found to be 60.2, one double bond requiring 61.6.

6. Artostenone is transformed into a saturated compound by catalytic hydrogenation with platinum black at 65–70°.

131. Investigations on the constitution of 'artostenone'.  
Part III. Reduction of artostenone to artostanone and artostenol.

M. C. NATH, Dacca.

1. Catalytic hydrogenation with platinum at 65°–70° saturates the double bond of artostenone, but retains the keto group unchanged.

2. Probability of the presence of the keto group in ring I, has been excluded; it has been suggested that the double bond in artostenone is in  $\alpha\beta$ -position with respect to the keto group.

3. Artostanone, the hydrogenation product of artostenone, has been isolated, m.p. 106°–107°.

4. Artostenone gives an oxime, m.p. 193–194°.

5. By method of reduction with sodium ethylate, the keto group is changed to hydroxyl, but the double bond remains intact. It has been proposed to call this product as artostenol.

6. Artostenol melts at 106.7° and its iodine value is 60.

7. Sodium amylate also reduces the keto group to hydroxyl.

8. The acetyl derivative of artostenol melts at 120–121°.

9. The acetyl derivative of the compound has m.p. 119–120°.

132. Investigation on the constitution of 'artostenone'.  
Part IV. Preparation of artostenamine and its complex with platinichloride.

M. C. NATH, Dacca.

1. Artostenone has been converted to an amine, artostenamine (m.p. 169–170°) through its oxime.

2. This amine is insoluble in strong hydrochloric acid but is soluble in glacial acetic acid.

3. Two molecules of this amine combine with one molecule of  $\text{H}_2\text{PtCl}_6$  to form a complex, artostenamine-platinichloride.

4. The molecular weight of this complex has been found by Pregl's micro-muffle method to be 1291.

5. From this the molecular weight of artostenone has been calculated to be 440.5 ( $\text{C}_{30}\text{H}_{50}\text{O}$  requiring 426 as the M.W.).

6. The platinum complex has C, 56.88 and H, 8.5% :  $(\text{NH}_2\cdot\text{C}_{30}\text{H}_{52}, \text{HCl})_2\text{PtCl}_4$  requires C, 57.05; H, 8.1%.

133. On Aristolochine, the principal alkaloid of the roots of *Aristolochia indica*, Linn.

P. R. KRISHNASWAMY and B. L. MANJUNATH, Bangalore.

This paper deals with the preliminary investigation on the constitution of *aristolochine*,  $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ , isolated from the roots of *Aristolochia indica*, Linn. (Krishnaswamy, Manjunath and Venkata Rao, *J. Indian Chem. Soc.*, 1935, 7, 476).

*Aristolochine* m.p. 215°;  $[\alpha]_D^{25}$ ,  $-\cdot 268.8^\circ$ , gives a mono-hydrochloride,  $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}, \text{HCl}$  (decomp. at 268°). It forms additive com-



pounds of the general formula  $(C_{17}H_{19}O_3N)_2.C_6H_5X$  (where  $X=H$  or  $Me$ ) with benzene and toluene. The molecule contains one methoxyl group, one active hydrogen atom and one dimethylamino group.

Further work is in progress.

134. Chemical examination of the roots of *Bragantia wallichii*.

P. R. KRISHNASWAMY and B. L. MANJUNATH, Bangalore.

A brief note on the preliminary investigation has already been communicated (Manjunath and Venkatasubbiah, *Proc. Ind. Sci. Congress*, 1930, 183). This paper deals with the further work on the subject.

The oil from the roots was found to consist mainly of the glycerides of palmitic, stearic and lignoceric acids, and of oleic, linolic and linolenic acids. Among the other products isolated, mention may be made of *iso*-aristolochic acid (*J. Indian Chem. Soc.*, 1935, 7, 476) and of a basic substance in the form of its hydrochloride. Attention is drawn to the fact that *Bragantia wallichii* belongs to the species of *Aristolochiaceae*.

135. Investigation of *Momordica charantia*, Linn. Part I.

N. K. SEN and B. K. BANERJEE, Dacca.

*Momordica charantia* (Karala in Bengali) in a finely powdered condition was extracted successively with various solvents.

Petroleum ether extract yielded a brown fatty residue which on saponification gave a mixture of fatty acids from which palmitic and stearic acids were isolated. From the unsaponifiable matter a sterol, m.p.  $132^{\circ}$ – $134^{\circ}$ , was obtained.

Ether and chloroform extracts contained mainly chlorophyll mixed with some fatty matter, from which nothing definite could be isolated.

Alcoholic extract yielded a bitter resinous substance which could be obtained in the form of an amorphous powder by repeated purification from a mixture of petroleum ether and chloroform. On hydrolysis it yielded a reducing sugar probably glucose, which gave an osazone, m.p.  $205^{\circ}$ , and an amorphous non-bitter aglucone indicating the glucosidic character of the substance. The bitter substance foams in aqueous solution and gives some of the characteristic properties of saponin.

Further investigation on this substance is in progress.

136. Isomerism of butane- $\alpha\beta\gamma\delta$ -tetracarboxylic acids.

P. C. GUHA and C. KRISHNA MURTHI, Bangalore.

The isomerism of the two (high and low melting) butane  $\alpha\beta\gamma\delta$ -tetracarboxylic acids and their derivatives has been discussed. Some new methods of their syntheses have been worked out.

137. *para*-Bridging of succinosuccinic ester.

P. C. GUHA, Bangalore.

In continuation and extension of the work reported (*Ind. Sci. Cong.*, 1936), the two bridged esters, m.p.  $112^{\circ}$  and  $132^{\circ}$ , respectively have each yielded more than one product on treatment with varying quantities of alcoholic potash. The action of oxidising agents such as permanganate and hypobromite is now described. Some synthetic experiments with a view to obtain the degradation products (by the action of alkali) are also described.



## 138. Synthetic production of terpineol from pinene.

B. G. S. ACHARYA and T. S. WHEELER, Bombay.

Attempts are being made to improve the proportion of terpineol by known methods through the intermediate preparation of terpin hydrate from pinene contained in turpentine. Pinene and dilute sulphuric acid are shaken vigorously when crystals of terpin hydrate are copiously formed. This reaction is found to be accelerated by the use of substances like gum arabic, turkey red oil, etc. which act as emulsifying agents. Terpin hydrate is then boiled with dilute oxalic acid when terpineol is formed. Preparation of terpineol through acetylation of pinene and subsequent hydrolysis of the resulting terpineol acetate gave poor yields.

## 139. Synthetical experiments in the thujane series. Part I.

P. C. GUHA, BHOLA NATH, and S. KRISHNAMURTHI, Bangalore.

By the modification of older method, it has been possible now to obtain quite an excellent yield of  $\alpha$ -methyladipic acid from *meta*-methylcyclohexanone. Ethyl  $\alpha$ -methyladipate has been converted into ethyl 3-methyl- $\Delta^1$ -cyclopentane carboxylate *via* the 2-keto and 2-hydroxy compounds. The action of diazomethane and diazoacetic ester upon the methyl cyclopentane ester under varying conditions is described.

## 140. Synthetical experiments in the thujane series. Part II.

P. C. GUHA, S. KRISHNAMURTHI, and BHOLA NATH, Bangalore.

In this paper are described the results of our experiments in the preparation of 1 : 3-dibromo-hexahydro-*p*-toluic acid starting from *p*-toluic acid, *via* *p*-toluic-3-sulphonic acid, 3-hydroxy-*p*-toluic acid, 3-hydroxy-hexahydro-*p*-toluic acid, 3-bromo-hexahydro-*p*-toluic acid. 1 : 3-Dibromo-1-methyl-cyclohexane-1-carboxylate is expected on treatment with zinc, to yield a compound possessing the thujane skeleton. 2 : 6-Dibromo-3-methyl-6-isopropyl-cyclohexan-1-one prepared from menthol *via* menthone, will be subjected to the same process of debromination with zinc, for the preparation of the corresponding compound isomeric with thujone.

## 141. Experiments towards the synthesis of derivatives of bicyclo- (0 : 3 : 3)-octane ring system.

P. C. GUHA and S. K. RANGANATHAN, Bangalore.

Having achieved the synthesis of *cis*-1-acetylcyclopentane-2-carboxylic acid (*Proc. Ind. Sci. Cong.*, 1936), some preliminary experiments were performed on the ring closure of its ethyl ester with sodium. The results obtained show that a 1 : 3-diketone is formed, isolable through its copper salt. Large amounts of the diketone are being prepared for a study of its properties. The work on the synthesis of *trans*-1-acetylcyclopentane-2-carboxylic acid along the lines adopted for the *cis*-acid has been described.

## 142. A resolution of bicyclo-(2 : 2 : 2)-octane-2 : 5-dione-1 : 4-dicarboxylic acid.

P. C. GUHA and S. K. RANGANATHAN, Bangalore.

The synthesis of bicyclo-(2 : 2 : 2)-octane-2 : 5-dione-1 : 4-dicarboxylic acid, starting from succinosuccinic ester, has been reported by one of us (*Current Science*, June 1936), and it was thought that a resolution of the acid would, in addition to its intrinsic interest, offer an additional proof of the correctness of its constitution. For this purpose the acid was



combined with brucine (2 molecules) when a salt separated. Specific rotation of the brucine salt after 5 recrystallizations was  $[\alpha]_D^{65} = -70.87$  ( $c=2.25$  in pyridine). The acid liberated from the salt had  $[\alpha]_D^{25} = +23.85$  ( $c=2.13$  in water). The mother liquor (of the brucine salt) yielded on three successive evaporation and filtration the pure salt of the *l*-acid which when liberated free had  $[\alpha]_D^{25.5} = -23.24$  ( $c=0.99$  in water). With the same thermometer the inactive, *d*- and *l*- forms were found to melt at  $268^\circ$ ,  $271^\circ$  and  $271^\circ$ , respectively.

#### 143. Experiments towards the synthesis of isofenchone and its derivatives.

S. K. RANGANATHAN, Bangalore.

Ethyl  $\alpha\alpha$ -dimethyl laevulate (ethyl mesitonate) b.p.  $108-110^\circ/25$  mm. has been condensed with zinc and ethyl bromoacetate to yield the lactone of ethyl  $\beta$ -hydroxy- $\beta\delta\delta$ -trimethyl adipate, b.p.  $137-38^\circ/6$  mm. The lactone was converted through the intermediate  $\beta$ -cyano- $\beta\delta\delta$ -trimethyl adipic acid to  $\beta\delta\delta$ -trimethyl-butane- $\alpha\beta\delta$ -tricarboxylic acid, m.p.  $169^\circ$ ; ethyl ester (alc. vapour method), b.p.  $125-28^\circ/1.2$  mm. The ethyl ester has been cyclised by sodium in benzene to the ethyl-cyclopentanone-5 : 5-dimethyl-2 : 3-dicarboxylate, b.p.  $158-161^\circ/3$  mm. Experiments are in progress for the confirmation of the constitution of the ketonic monocarboxylic acid obtained from the above by hydrolysis followed by decarboxylation.

#### 144. Synthesis in the carane series.

P. C. GUHA and D. K. SANKARAN, Bangalore.

The sodium derivative of Guareschi imide on being condensed with tetramethylenedibromide gave the imide of 1 : 1-dimethyl-2 : 6-dicyano-cycloheptane-2 : 6-dicarboxylic acid, m.p.  $303^\circ$ . Hydrolysis of the product with  $1\frac{1}{2}$  per cent. sodium hydroxide gave a nitrogenous compound m.p.  $250^\circ$  which on further hydrolysis with 15 per cent. sodium hydroxide yielded cycloheptane-2 : 2 : 6 : 6-tetracarboxylic acid. The above tetra basic acid, on decarboxylation at  $130-140^\circ$  gave cycloheptane-2 : 6-dicarboxylic acid (I), m.p.  $134-135^\circ$ .

The  $\alpha\alpha$ -dibromo derivative of (I) is expected to give apocarane dicarboxylic acid (II) on treatment with zinc.

#### 145. Synthesis in the pinane series. Part III. Towards the synthesis of pinocamphone and nopinane.

P. C. GUHA, K. GANAPATHI, D. K. SANKARAN, and  
V. K. SUBRAMANIAN, Bangalore.

The syntheses of isonopinone, nopinane and also pinocamphone, which will amount to a total synthesis of  $\alpha$  and  $\delta$ -pinenes, have been investigated as follows: The diethyl ester of the *trans*- or *cis*-norpinic acid is reduced by means of sodium and absolute alcohol to the same glycol (cf. Ostling, C., 1921, 3, 105), a very viscous liquid, b.p.  $125-128^\circ/4$  mm., which (shown to be of the *trans*-configuration) by the action of  $\text{PBr}_3$  yields the di-bromide, b.p.  $100-102^\circ/4$  mm. With KCN in alcoholic solution, the dibromide gives the dicyanide, b.p.  $142-45^\circ/6$  mm., which on hydrolysis with aqueous potash furnishes in good yield *sym*-homopinic acid (I), m.p.  $120-21^\circ$ , (dianilide, m.p.  $216-217^\circ$ ). It is expected



to possess the *trans*-configuration. The diethyl homopinate, b.p. 133-135°/3 mm., by the action of sodium in xylene solution yields a product exhibiting the properties of a  $\beta$ -ketonic ester (II). The conversion of (II) into (a) isonopinone (III) (by hydrolysis and decarboxylation), (b) nopinane (IV) (by reduction of the latter), and (c) pinocamphone (V) (by decarboxylation of the methylated product) are in progress.

The bicyclic compounds obtained in this series are expected to be of the *trans*-series, while those found in nature are all of the *cis*-type. The isomerism and the significance of this work from the point of view of the Sachse-Mohr theory are discussed.

146. Studies on optical activity and chemical constitution of optically active bases and acids. Part IV.

MAHAN SINGH and H. B. DUNNICLIFF, Lahore.

Camphor has been condensed with dimethylaminobenzaldehyde and camphoric anhydride and oxymethylene camphor have been condensed with dialkylaminoanilines.

*p*-Dimethylaminobenzylidene camphor has  $\alpha_D = 731^\circ$ , whereas benzylidene camphor has only  $\alpha_D = 425^\circ$ .

*p*-Dialkylaminocamphoranilic acids have been examined polarimetrically in various solvents. There is no definite order in which the dialkylamino groups can be arranged. The compounds in some cases are also examined in the presence of hydrochloric acid and in every case a slight increase is recorded.

The dialkylamino groups have brought a very small change in the rotation constants of anilinomethylenecamphor.

147. Asarone.

K. S. SUBRAMANIAN and B. SANJIVA RAO, Bangalore.

The liquid asarone from *Acorus calamus* gives the same pseudonitrosite as solid propenyl asarone. The liquid gave 10 per cent. yield of solid dibromide while the solid gave 50 per cent. of the same dibromide. Potash fusion of the liquid gave an excellent yield of the solid asarone. The liquid appears to be a mixture of *cis*- and *trans*-propenylasarone.

148. Experiments on the synthesis of new local anæsthetics.

K. N. GAIND, J. N. RAY, and A. WAHAB, Lahore.

A detailed study has been undertaken to establish the factors which impart local anæsthetic property to a compound. In this connection, the condensation products of  $\alpha$ -hydroxy- $\beta$ -chlorobutyric esters with piperidine have been acylated with various acids. The ester grouping has also been varied from methyl up to butyl. All the compounds possess very strong local anæsthetic property as tested by the rabbit's cornea method and give stable sterilizable salts. The condensation product of two molecules of piperidine with one molecule of epichlorohydrin has also been prepared. The resulting compound has been acylated with various acids and the properties of the products studied. In every case there is a strong local anæsthetic action observable.

149. Condensation of furil and furoin.

A. C. SIRCAR and S. C. GUHA, Calcutta.

Benzil and benzoin are very well adapted for various types of condensations (Japp and Hooker, *J.* 1884, 672; Japp and Robinson, *J.* 1882, 326; Anscutz and Geldermann, *J.* 1891, A, i, 725; Japp and Murray,



*J.* 1894, 889 ; Japp and Meldrum, *J.* 1899, 1037, etc.). Many of these condensation products are very interesting both from the theoretical as well as practical point of view. It was, therefore, expected that the heterocyclic compounds furil and furoin would also yield a series of similar condensation products. In the present paper a large number of such condensation products has been described.

150. Photosensitising dyes. The preparation of the alkiodides of picoline and their subsequent condensation with *p*-dimethylaminobenzaldehyde.

M. Q. DOJA, Patna.

Mills and Pope (*J.* 1922, 121, 946) prepared 2-*p*-dimethylamino-styryl-pyridine-methiodide by the interaction of  $\alpha$ -picoline methiodide and *p*-dimethylamino-benzaldehyde. This compound was found to be a powerful sensitiser for green light, a region for which it is usually difficult to get a suitable sensitiser. It was expected that the photographic characteristics of this compound will change with the nature of the alkyl radical attached to the quaternary nitrogen atom. With a view to a systematic investigation of this problem, the ethyl, propyl, butyl and amyl iodides of  $\alpha$ -picoline have been prepared and condensed separately with *p*-dimethylaminobenzaldehyde. In each case a new photosensitising dye has been obtained.

151. Simultaneous determination of chlorine, nitrogen and arsenic in organo-arsenic compounds.

H. N. DAS GUPTA, Calcutta.

No method is as yet known the adoption of which would lead to the simultaneous determination of the above three elements. The present method consists in digestion of organo-arsenic compounds containing chlorine or nitrogen or both in a mixture of sulphuric acid and potassium sulphate with a small amount of metallic selenium. The digestion requires about 45 minutes for completion. The halogen is evolved as hydrochloric acid which is absorbed in alkali and estimated. The nitrogen is liberated as ammonia on treating the cooled digest with alkali and the residual arsenic is estimated iodometrically.

152. Tannic acids from myrobolan.

S. R. SUNTHANKAR and S. K. K. JATKAR, Bangalore.

The following acids were prepared in a pure form from myrobolan extract previously reported: elagic, elagitannic, chebulinic and gallic. The various physico-chemical constants of these acids such as optical activity, dispersion and basicity (as determined by the potentiometric methods developed in our laboratory) were compared with the similar properties of Kahlbaum and E.de Haen samples. The properties of inks prepared from these acids are also reported in this paper.

## Industrial Chemistry

153. The fastness of the naphthol colours. Part I.

R. B. FORSTER, P. R. MEHTA, S. R. RAMACHANDRAN, and  
K. VENKATARAMAN, Bombay.

About 20 per cent of the synthetic dyestuffs consumed by the Indian textile industry being represented by the insoluble azo colours, the



fastness of the prevailing combinations has been studied. The experiments on kier boiling have been conducted in a small and specially designed pressure kier in which the conditions approximated to those in technical practice. The dye-stuff on the fibre was estimated in terms of the nitrogen content. A new technique has been developed for studying the fastness to rubbing, employing a Kleinewefers yarn mercerising machine. No linear relationship could be traced between the substantivity of a naphthol and the fastness of a dye derived from it. Since, however, substantive naphthols in general lead to comparatively fast dyeings and since symmetrical structure in a naphthol is favourable to substantivity, new and symmetrically constituted members of the Naphthol AS series have been prepared. The factors governing fastness to rubbing are discussed. Thus it is shown that the replacement of a stabilized diazo salt by a freshly diazotized solution of the base is not always an advantage. The addition of formaldehyde to the naphtholating bath increases rubbing fastness. The influence of the concentration of the after-treatment soap solution and of the time of soaping has been quantitatively examined. The rubbing fastness of the same combination is not identical in the case of cotton and viscose, and the difference is not always in the same direction for various combinations.

#### 154. The interaction of diazo salts with silk.

R. B. FORSTER, S. R. RAMCHANDRAN and K. VENKATARAMAN,  
Bombay.

The tyrosine of the silk fibre couples with diazotized amines to give dyeings of yellow and brown (compare Sisley *et al.*, 1931). Using the stabilized diazo salts, shades ranging from old gold to deep reddish and olive browns have now been obtained; buffering is essential for the production of full shades. The dyeings are characterized by fastness to washing. By dyeing silk with direct, basic or acid colours containing free amino groups and after-treating with nitrous acid, a large range of fast and attractive shades is available. Beautiful two-colour effects are produced by treating unions of silk and cotton or silk and viscose with a stabilized diazo salt or by dyeing a solid shade with a substantive colour and after-treating with nitrous acid.

The mechanism of the action is discussed.

#### 155. Sugars in mohua flowers.

D. G. WALAWALKAR, Waltair.

The reducing and non-reducing sugars have been estimated and an attempt has been made for the preparation of a solid product out of the mohua syrup.

#### 156. Furfural and other by-products from water hyacinth.

SASANKA DEY and H. K. SEN, Ranchi.

Recently a mass eradication by manual collection of water hyacinth (*Eichornia crassipes*), spreading, according to an official report, over an area of 4269 sq. miles in the lower districts of Bengal, has been emphasized upon. How far the pest can be combated in this way remains to be seen. In any case, the utilization of the weed would lead to the winning of certain important technical products, for which there is already demand in this country, and future development of interdependent industries can also be visualized. It is calculated that there are at least 107 million tons of green or 5.3 million tons of air-dried hyacinth in Bengal, which can yield 0.3 million tons of furfural, 0.53 million tons of potassium



chloride, 56 million gallons of alcohol, 0·8 million tons of acetic acid, 0·18 million tons of acetone, and 2·12 million tons of compressed fibre.

Methods of technically separating the different products have been described, and balance sheet supplied. Furfural can be produced at 3 annas per pound, whilst the prevailing price in large bulks in America is 10 cents.

### 157. Fuel consumption in sugar factories. Part I.

M. R. MANDLEKAR, Bangalore.

As an outcome of an investigation into the problem of extraneous fuel consumption (e.g. wood and coal) in sugar factories, the chief sources of the loss of thermal efficiency of the boiler installations have been found to be :

1. Unsystematic methods of feeding 'bagasse' on to the step-grate furnaces resulting in fluctuating furnace conditions.
2. Uncontrolled admission of cold air to furnaces causing (a) reduction of combustion temperature, and (b) incomplete combustion of fuel.
3. Hot gases which leave the flues at a sufficiently high temperature (usually over 550°F.).
4. Other sources, e.g. exhaust steam, radiation losses, steam leakages, multiplication of working units with high capacities for heat, etc.

### 158. Fuel consumption in sugar factories. Part II.

M. R. MANDLEKAR, Bangalore.

The following remedies have been found to have successfully overcome the loss of efficiency occurring through various sources, and extraneous fuel costs can be reduced to an appreciable extent :—

1. A special design of the boiler furnace for wet bagasse (50% moisture) is necessary, slope of the grate being nearly 55°. Combustion chamber should provide a drying zone for bagasse before the fuel catches fire. The products of combustion should be required to travel just enough length of furnace and at such velocity as would enable the deposition of ash and suspended material to be kept back. Mechanical stoking arrangements are used with great advantage in large installations.
2. Enough exhaust steam is available to heat feed water and therefore economizers can conveniently be replaced by arrangements for heating the air required for combustion. Waste heat of the flue gases can thus be returned to the furnace. Air requirements of the fuel should be adjusted according to the CO<sub>2</sub> content of the flue gases, which should be 10–12% for bagasse. By pre-heating the air to 300°F. alone, thermal efficiency can be increased by over 12%. Arrangements for forced draught will be necessary and the cost of the extra height of the chimney could be saved.
3. By establishing a scientific control of the installation and various operations involved, most of the losses could be minimised. Efficiency figures with bagasse boilers have reached well over 70%.
4. Molasses—hitherto regarded as a waste product—can be successfully burnt in fire-tube boilers with steam atomizing effecting a saving of nearly 30% of extraneous fuel (coal).

### 159. Manufacture of soft sugar by using invert syrup from cane-sugar solutions.

S. D. AGNIHOTRI, KOLHAPUR.

Experiments are undertaken to manufacture soft sugar by using syrup prepared from the Globe Glucose 5A of the Corn Products Co. (India), Ltd. The author compared the soft sugar samples with those



prepared by using the syrups prepared from sulphited clear cane juice, cane syrup and crystal sugar. Syrups were prepared by inverting the solutions with sulphuric acid, neutralizing with calcium carbonate and concentrating under atmospheric pressure. The syrups were a bit coloured. The density of the syrups was 34 and 37 Baume.

Different sugars such as wet third sugar from the centrifugals, sieved sugar and ground sugar were tried, of which the first was found most suitable. The soft sugars obtained by the use of invert syrups were definitely superior to those by the use of Globe Glucose syrups in feel and moisture retaining capacity.

Further work is in progress.

#### 160. Utilization of waste cane molasses. Part I.

S. K. GHOSH and R. C. RAY, Patna.

The cane sugar molasses contains a certain amount of nitrogenous matter (which is present chiefly in a colloidal state) sucrose, reducing sugars, inorganic salts and colouring substance. The latter probably exists in the form of adsorption compounds of the nitrogenous colloids. It is suggested that molasses can be used for making syrups for drinking purposes and for the preservation of fruits and for preparing artificial honey. The present paper describes experiments for removing colouring matter and the undesirable mineral salts so as to make molasses suitable for the purposes mentioned above.

#### 161. Utilization of waste cane molasses. Part II.

S. K. GHOSH and R. C. RAY, Patna.

It is well known that molasses contain a large amount of potassium salts which impart to them a bad taste and render them unfit for consumption by animals. Attempts have been made to recover the potassium salts by the permutite process. The present paper also describes certain experiments carried out with a view to recover the sugars present in the molasses by solvent extraction.

#### 162. Studies on ligno-cellulose.

P. N. SENGUPTA and H. K. SEN, Calcutta.

In this investigation the behaviour of lignins obtained from different sources under identical reaction conditions was studied. The sources of the lignins were: (1) *Excoecaria agallocha* (vernacular Gangwa) saw dust, (2) dried water hyacinth, and (3) rice straw. For the extraction, 72% sulphuric acid was used. Lignins were washed completely acid-free. Pure cellulose was also extracted from the same sources by the chlorine peroxide process. The ash contents of the lignins, methoxyl and acetyl groups before and after exhaustive methylation and acetylation were determined. They were nitrated and chlorinated and the soluble and insoluble extracts were examined. These results indicate that under the same conditions the lignins from different sources do not behave identically.

#### 163. Mechanism of the reaction of acetylation.

L. THORIA and N. AHMAD, Matunga.

Experiments were carried out in order to determine if a diacetate was formed in the course of acetylation of cellulose, which always results into a triacetate. Acetone solubility was regarded as a test for the presence of diacetate. Work done so far on cellulose swollen with acetic acid shows that a diacetate is formed during the reaction and that it is



considerably increased in quantity, if the following changes are made in the process :—

- (a) Mercerization of cellulose before swelling with acetic acid.
- (b) Lowering of reaction temperature.
- (c) Reduction in the quantity of catalyst.
- (d) Addition of catalyst to the swelling acetic acid.

It is believed that it might be possible by proper adjustment of the conditions of acetylation to arrest the reaction at a stage when the whole of the reaction product is soluble in acetone. The solution of the problem seems to lie in the following direction :

- (i) Diffusion velocity of the reaction mixture should be increased by suitable swelling agents to such an extent that the scene of reaction is shifted completely from the surface of the fibre to the micelle.
- (ii) The reaction velocity should be kept at such a low level, as would favour the formation of a diacetate, by adjusting the temperature and the quantity of the catalyst.

#### 164. A note on the fixed oil from *Anona squamosa* (custard apple) seeds.

M. GHOUSE MOHIUDDIN, Hyderabad (Deccan).

The kernel of the fresh seeds (reputed to be a good vermicide or insecticide) on continuous extraction with hot high boiling petroleum ether yielded a pale-yellow semi-viscid, odourless oil, (10%) soluble in ether, acetone, petroleum ether, chloroform, benzene, carbon bisulphide and hot absolute alcohol. Besides the physico-chemical constants—sp. gr., acid number, saponification value, iodine value, Reichert Meissl value, acetyl value, viscosity, refractive index, specific rotation, absorption spectrum, a number of colour reactions have been studied. No alkaloid could be detected in the seeds though leaves have been reported to possess an alkaloid in traces. Further work on the nature of the fatty acids is in progress.

#### 165. A new method of making transparent toilet soap without the use of sugar.

N. G. CHATTERJI, Cawnpore.

The soap stock is rapidly saponified with stoichiometric quantities of very strong alkali solution and then rectified spirit is added to the hot soap gel to keep the whole in the transparent peptized condition even after cooling.

#### 166. Detergent action of soaps.

B. S. KULKARNI and S. K. K. JATKAR, Bangalore.

In continuation of our work on the detergency of the soap solutions, experiments are extended to the series of potassium soaps, with regard to the interfacial tension, deflocculating power, viscosity and emulsifying power of the solutions. Deflocculation experiments with Fuller's earth, as considered along with the other properties of the soap solutions like viscosity and interfacial tension, correspond very closely with the detergent actions of the solutions; the Fuller's earth may therefore be considered as an ideal dirt in the detergent action of the soaps.



## 167. Studies in the saponification of oils.

N. G. CHATTERJI and R. K. GOBHIL, Cawnpore.

The kinetics of the saponification of *Mohua* oil and the influence of strength of alkali, temperature, rate of stirring, and the original acidity of the oil, on the chemical reaction have been studied in detail. Many interesting results have been obtained, the most important being the extremely rapid and practically complete saponification under certain conditions, of the oil by alkali even when stoichiometric quantities are taken. Attention is drawn to the application of these results in the manufacture of good quality soap.

168. Industrial utilization of the oil from *Pongamia glabra*.

C. R. N. REDDY, Waltair.

Possibilities of utilizing this oil for soap-making and as a lubricant have been investigated. It yields a fairly hard soap with good washing properties comparable with that of cocoanut oil but the lather is close and gummy. Good washing soap is obtained with 25% of oil.

The following constants obtained show that the purified oil is a good lubricant for heavy lathes, gears and chains.

Flash point	..	..	..	400°F.
Pour test	..	..	..	46.4°F.
Viscosity	..	284.36 sec.	at 85°F ;	140 sec. at 120°F.
Chemical action	..	..	..	nil

It shows no tendency to become gummy as castor oil does.

## 169. Utilization of oils from roasted cashewnut shells.

N. M. PATEL and M. S. PATEL, Bombay.

About 28,000 tons of raw cashewnuts are roasted every year in India for the production of cashewnut kernels. 100 lbs. of nuts give about 40 lbs. of roasted shells containing nearly 18 per cent. oil. These shells are at present thrown away or just burnt. At the present rate of kernel production nearly 11,000 tons of roasted shells which could yield 2,000 tons of oil are available.

The oil from the roasted shells has been extracted by solvent extraction process and its physical and chemical constants have been determined. Drying tests have been carried out. Films with and without the incorporation of driers were prepared on the clean surfaces of glass, copper, tin plate, aluminium, galvanised iron and iron and the time required to dry them at room temperature was determined. The oil was acetylated and the drying properties of the product have been studied.

It has been found that cashewnut oil is not triglyceride of fatty acids but a mixture of a hydroxy acid of the aromatic series and a polyhydroxy phenol. The rate of drying varies with different surfaces and also varies with temperature. Dry films of ordinary oil were subjected to the action of hot and cold dilute acids, dilute alkalies and dilute alcohol. Dried films of the oil resist the action of cold dilute acids as well as that of hot and cold dilute and concentrated hydrochloric acids. The films are fairly resistant to the action of cold dilute alkalies and alcohol.

The acetylated oil gives films of lighter colour and are affected less by acids and are less resistant to alkalies. The acetylated oil films dry more quickly than ordinary oil. The acetylated oil films resist well the action of dilute and concentrated hot and cold hydrochloric acid.



## 170. A simple apparatus for the analysis of hydrogen.

S. K. K. JATKAR and V. T. ATHAVALA, Bangalore.

A simple apparatus for determining the purity of hydrogen used for hydrogenation of oils is described. The accuracy is 1 part in 10,000.

## 171. Continuous hydrogenation of oils by catalysts of nickel and its alloys.

V. T. ATHAVALA and S. K. K. JATKAR, Bangalore.

The measurements of the activity of the electrolytically oxidized nickel wire showed that its activity is less than that of the supported catalysts like those prepared from Kieselghurcarbonate. Life test of the catalyst showed a stepwise fall in the activity which fell down to 50% in five days. Unlike the Kieselghur catalysts, the wire catalyst has no maxima in activity up to 210. The activity of monel (75 Ni : 25 Cu) wire is equal to that of nickel wire with the advantage that it can be reduced at a lower temperature. The 'ferry' (54 Ni : 46 Cu) has considerably lower activity. Raney catalysts did not give promising results. It was observed that shutting down for a few days always resulted in the disintegration of the catalyst surface. This has been shown to be due to the peculiar property of the various saturated glycerides which show dimorphism, the stable form having markedly lower density.

## 172. Selective hydrogenation of oil.

S. K. K. JATKAR and V. T. ATHAVALA, Bangalore.

Some important observations have been made in the study of hydrogenation of oils in presence of different preparations of nickel catalysts. Each active centre on the catalyst appears to have its own optimum temperature. This is prominently shown by a step out in the temperature coefficient of catalytic activity, and by its own characteristic heat of activation. The question of selectivity of hydrogenation of the different glycerides has been also studied by investigating the curve of iodine value and refractive index, and thiocyanogen value and refractive index, in the course of hydrogenation. Perhaps the most valuable result of this investigation is the vindication of the superior activity of the precipitated catalyst, over other catalysts including those of Lush and Raney; large difference found in commercial practice having been now shown to be due to the change in the method of operation. The precipitated catalyst can now be prepared in a suitable form for commercial purposes and subsequently activated with the same ease as the wire form of catalyst and can be used with existing plants with very little alteration.

## 173. Continuous hydrogenation of oils by precipitated catalysts.

V. T. ATHAVALA and S. K. K. JATKAR, Bangalore.

We have studied the comparative activity of nickel catalysts prepared from (1) precipitated nickel carbonate, (2) nickel carbonate-Kieselghur, (3) nickel hydroxide-silica gel and (4) nickel peroxide-Kieselghur for the hydrogenation of groundnut oil in a continuous process. Although the activity of (1) is the highest, it cannot be used owing to considerable shrinkage on heating. The catalysts, (2) and (4) are far superior to any other catalyst. The preparation of (4) is inconvenient. The life test of catalyst (2) and (4) showed that in the case of (2) there was periodic rise and fall till the activity fell to 85% after continuous run of ten days, while (4) showed a stepwise fall in the activity to 50% in seven days with the same sample of oil.



## 174. Studies in the oxidation of linseed oil.

N. G. CHATTERJI and A. C. GUPTA, Cawnpore.

The rate of oxidation of linseed oil refined in different ways has been directly studied from the rate of absorption of oxygen. The possibility of the application of these results in the paint industry is discussed.

## 175. Spectrographic studies of ghee.

HABIB HASAN, S. R. BHATE, and N. N. INUGANTI, Hyderabad.

Absorption spectra were taken of samples of pure cow and buffalo ghee, adulterated ghee and hydrogenated groundnut oil, characteristic graphs for each will be shown.

## 176. Supply of ghee in the town of Hyderabad.

S. R. BHATE and HABIB HASAN, Hyderabad.

An examination of the supply of ghee in the town of Hyderabad revealed 53% of the samples examined to be adulterated to the extent of 80% and over; 10% of the samples were adulterated to the extent of 60% and only 27% were found to be genuine. Certain modifications in the methods of examination of ghee samples have been worked out.

177. Chemical examination of the solid residue which separates from the oil of the seeds of *Pongamia Glabra*.

B. L. MANJUNATH and A. SEETHARAMIAH, Bangalore.

The solid was repeatedly washed with methyl alcohol in order to remove resinous products. The residue was found to consist principally of Karangin (Beal and Katti, *Chem. Zentr.*, 1926, II, 596; Limaye, *Proc. Ind. Sci. Congress*, 1925, 118), and this could be completely extracted in a soxhlet by boiling alcohol. The residue was found to consist of the zinc salt of behenic acid. This fact is interesting because Sudborough *et al* (*Jour. Ind. Inst. Sci.*, 1923, 6, 93) during the course of a detailed analysis of the oil were unable to obtain behenic acid.

In addition to these materials, a very small amount of a crystalline body, yellow in colour, was obtained from the alcoholic filtrates.

Karangin is acted upon by light and is rapidly converted into an orange-yellow material. However, this colour disappears on crystallizing the substance from alcohol. But, under certain conditions an orange compound, m.p. 125°, is formed. The nature of this change is under investigation.

## 178. Some local essential oils.

HABIB HASAN and S. R. BHATE, Hyderabad.

The physical constants and chemical constituents of some of the locally found essential oils have been determined. The methods of obtaining them in quantities have been worked out.

## 179. On sandal seed oil.

P. R. KRISHNASWAMY, M. K. MADHURANATH, and B. L. MANJUNATH, Bangalore.

The sandal seed oil has been the subject of several investigations in recent years (Iyer, *Analyst*, 1935, 319; Sreenivasaya and Narayana, *Jour. Ind. Inst. Sci.*, 1936, I, 1(A), etc.). The present paper deals with the systematic and complete analysis of the oil.



The seeds contain about 45 per cent. of a thick, viscous oil. On saponification, a large quantity (13 per cent.) of a white, sticky, resinous mass is thrown down.

The liquid acids were found to consist of oleic acid (54 per cent.) and linolenic acid (6 per cent.). The only solid so far isolated is highly unsaturated, and appears to have the formula  $C_{18}H_{30}O_2$ .

The paper deals with the constitution of this acid.

180. Essential oil from *Spheranthus Indicus*.

(MISS) MARY MATHEN and B. SANJIVA RAO, Bangalore.

The volatile oil having an agreeable odour was obtained in a yield of 0.3 per cent. from the shrub. It was found to contain  $\alpha$ -phellandrene, a bicyclic sesquiterpene and a mixture of tertiary sesquiterpene alcohols belonging to the eudalin group.

181. Paper-pulp fibres of Hyderabad State.

K. NIZAMUDDIN, Hyderabad.

The paper deals with the results of experiments carried out with various raw materials such as bamboos, castor stalks, linseed stalks and kopri grass, etc. found in Hyderabad State.

182. A study of desizing action.

R. B. FORSTER, M. R. JAMBHEKAR, and K. VENKATARAMAN, Bombay.

The use of amylolytic enzymes for the removal of size in cloth ('steeping') prior to kier-boiling and bleaching being common practice in bleachworks, an examination of the factors governing the process of desizing has been made. The problem has been approached from two angles: (1) the comparative efficiency of the four main types of products recommended for desizing: (a) organic chloro compounds which chlorinate and partially solubilize the starch, (b) diastases, (c) mould enzymes, and (d) bacterial enzymes; and (2) the influence of the constituents of sized cloth and of the conditions of the desizing bath on the degree of desizing achieved.

The course of the starch degradation was followed by noting the reducing power and the viscosity.

The seven commercial desizing agents, chosen as representative of the best known products on the market were first examined with regard to their reducing power.

With a solution of the desizing agent of the order used in mill practice three of the diastases and the bacterial enzyme converted the paste into a clear limpid liquid, while one of the diastases actually increased the viscosity. With regard to saccharifying power, wide variations were noticed among the different agents.

The hydrolysis with the diastase was initially less rapid than with the bacterial enzymes but at the end of 2-3 hours they were equal, the conversion of the starch being nearly complete in the time.

The action of the same enzyme on different starches disclosed that, with the small concentration of enzyme employed, the starches were saccharified to quite different degrees, but the liquefactions as indicated by the viscosities were identical.

Not only is there no advantage in adding any of the common 'wetting agents' to the desizing liquor, but it is definitely detrimental.

Of the metallic salts (e.g. salts of calcium, copper, iron, lead, magnesium, zinc) likely to occur in cotton fibres, all except calcium chloride were found to be unfavourable to the action of the enzyme, several



effecting total inhibition, even in minute concentrations. With the exception of salicylic acid, the common antiseptics in size mixtures were innocuous with regard to the liquefaction of the starch, but the saccharification was in some cases adversely affected. Since coloured goods are desized before boiling and bleaching, the possible deactivation of the amylase by dyestuffs has been studied with a variety of vat and naphthol colours.

The influence of various other factors on the course of desizing is also described.

### 183. Wetting agents in textile processing. Part I.

D. R. DHINGRA, I. S. UPPAL, and K. VENKATARAMAN, Lahore.

It is well known that the sodium salts of alkyl hydrogen sulphates (e.g. sodium lauryl sulphate) are powerful wetting and emulsifying agents. An improvement has been the preparation of aliphatic compounds in which an amino group condensed with a long chain fatty acid and a sulphonic group attached to a carbon atom are present. Textile auxiliaries with augmented wetting, emulsifying, cleansing and level dyeing properties have now been obtained by the interaction of oleic or ricinoleic acids or their chlorides with sulphanilic or naphthionic acids or their N-alkyl (and particularly the N-methyl) derivatives. The main features of the preparation of these compounds are : (1) the use of ricinoleic acid in which the free hydroxyl group aids the lowering of the interfacial tension between the solution of the substance and fatty matter (such as those present in grey yarn and cloth), and (2) the utilization of sulphanilic and naphthionic acids which are common dyestuff intermediates. The reaction is carried out in general by treatment of the fatty acid chloride with the sulphonic acid of the aromatic amine in a suitable basic solvent such as pyridine ; the condensation products are finally converted into the sodium salts. In the case of ricinoleic acid, the hydroxyl group is initially protected by acylation, e.g. by acetylation, the protecting group being removed during the condensation of the acid chloride with the amine or during the later treatment of the product with water or with aqueous acid or during the final conversion into the sodium salt. Other wetting agents are obtained by the further sulphonation of the above oleyl and ricinoleyl amides. Aqueous solutions of these soaps are not precipitated by hard water. The substances are useful in kier-boiling (since they have wetting, emulsifying and detergent properties), as an aid to penetration in mercerization, as additions to the dye-bath leading to level-dyeing (since the substances are protective colloids), as stabilisers for hydrogen peroxide solutions, and as general auxiliaries in textile processing. The magnesium and aluminium salts of the above sulphonic acids are useful, by themselves and in conjunction with sodium silicate or metaphosphate, for stabilising hydrogen peroxide bleach liquors.

### 184. Injection moulding of shellac compositions.

S. RANGANATHAN and R. W. ALDIS, Ranchi.

In the 'Injection Moulding' process, the moulding material is preheated in a closed cylinder and then squirted under pressure into a cold mould. Special advantages of the process are : (a) speed of production, (b) freedom from 'sticking in the mould' and (c) very low rate of mould wear.

A shellac mixture suitable for moulding by the injection process has been formulated and a suitable type of apparatus has been devised.



## 185. A technical process for washing and refining of stick lac.

A. K. THAKUR, Ranchi.

Seedlacs as prepared in India often have adhering oxidised lac-dye and nitrogenous matter, both of which react deleteriously in the application and processing of such seedlacs. The consumer of lac requires 100% resin in his lac products, for otherwise the materials behave erratically more especially when used in protective coatings and in electrical insulation. A technical method has been worked out, by which the impurities in the crude material can be eliminated. It consists of :—

- (1) grinding slowly the stick lac in a ball-mill in presence of dilute solutions of potash alum or tri-ethanolamine or other suitable reagents, which help to dissolve the dye and other soluble matter. They are removed by repeated process of decantation, leaving washed resin in the mill.
- (2) The powdered lac is further purified by immersing in saturated solution of sodium chloride. The lac resin floats on the surface while the impurities settle at the bottom. This is very efficiently accomplished by means of 'Sharple's Super Centrifuge'.

## 186. Estimation of orpiment in shellac.

M. RANGASWAMI, Ranchi.

A method for estimating the orpiment content of shellac has been published by this Institute (Bulletin No. 7 Indian Lac Research Institute, 1932, p. 2). The methods generally in vogue take long time and the use of large quantities of shellac for digestion with fuming acids evolving large volume of fumes. The possibility of using smaller quantities of samples and thus shortening the time required for an analysis without detracting from accuracy, has been investigated.

Careful mixing and fine grinding before sampling are necessary for accurate results. The usual iodometric method with N/50 or N/100 iodine solution is followed. An apparatus for digesting several flasks at a time has been devised, in which the use of suction can be obviated, and the fumes adsorbed.

	Found percentage of $As_2S_3$
Modified American method as followed by the Indian Lac Research Institute, using 10 gms. of shellac ..	0.92, 0.91, 0.91.
The present method using 0.5 gm. of shellac .. ..	0.94, 0.91.
The present method using 1.0 gm. of shellac .. ..	0.89, 0.90, 0.89, 0.91, 0.94.

## 187. A new method for the iodine value of shellac.

M. VENUGOPALAN and H. K. SEN, Ranchi.

The iodine value of shellac is used to estimate the resin content. In America the method of Wij's has been adopted as standard. This method is not entirely satisfactory, and one of the objections to the method lies in the difficulties associated with the preparation of the Wij's reagent which is also rather tedious. A means of overcoming the difficulties of preparation of the reagent has been indicated by Hunter and Hyde ('The Analyst' LVIII, No. 690, p. 523, 1933). These authors use equivalent amount of potassium iodide and toluene-*p*-sulphondichloramide dissolved in glacial acetic acid.

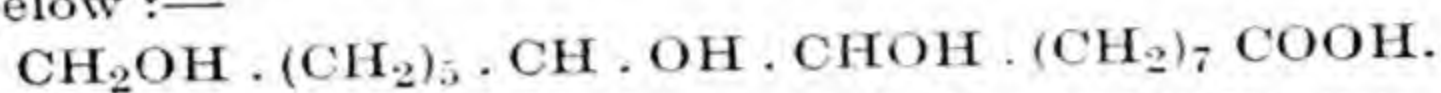


In this laboratory, the action of *p*-tolyl-iodochloride dissolved in acetic acid on shellac has been investigated with a view to develop a 'chlorine value' of shellac. This method gives results of the same order as by the Wij's method, and it has also been extended to certain oils.

#### 188. Separation of aleuritic acid from shellac.

N. N. MURTI, R. W. ALDIS, and A. K. THAKUR, Ranchi.

Aleuritic acid is the largest constituent of the mixture of hydroxy acids which go to form shellac (Harries and Nagel *Wiss. Veroff. Siemens-Konzern* 1, part 3, pp. 178-181). Its constitution has been established as trihydroxy palmitic acid, and the disposition of the hydroxyl groups are shown as below :—



The possibility of utilizing this acid in the manufacture of synthetic resins, in medicine and as a means of modifying shellac by increasing the aleuritic acid content has been indicated, and accordingly methods for quickly and cheaply isolating this constituent of shellac have been investigated.

Amongst the new methods which have been evolved, the following are promising : (a) mild oxidation, to break down the unsaturated acids leaving the aleuritic acid in a comparatively free condition ; (b) fractional solubility of the hydrolysed shellac acids ; and (c) 'salting-out' by addition of sodium chloride to a solution of shellac in 5N-caustic alkali. In all instances, aleuritic acid of good purity and yield is obtained.

#### 189. Preparation of 'hard lac resin'.

M. VENUGOPALAN and H. K. SEN, Ranchi.

Shellac from which the soft, ether-soluble resin has been removed shows improved properties for certain uses. Methods for preparing this resin which avoid the expensive and troublesome process of direct ether extraction are being investigated. Verman and Bhattacharya (Tech. Paper No. 1, 1934, London Shellac Research Bureau) have published a toluene extraction method which retains 10-15% of the soft resin, but which is reported to be quite satisfactory for the purposes for which this hard resin is used. Our object has been to separate the hard resin in a much purer condition : (a) by the reaction of urea with an acetone solution of shellac, which polymerizes the hard resin, leaving the soft resin in a condition easily extractable by acetone. This process removes the soft resin practically completely without affecting the hard resin which is now polymerized. The polymerized hard resin can be easily depolymerized by boiling with water which also removes the urea. (b) A second method has also given promise which consists in precipitating the hard resin from an acetone solution of shellac by dropping it on ether and vigorous stirring. The precipitated hard resin is washed once or twice with ether, and the mixed solvents are used in a counter-current for further precipitation. The solvents are ultimately recovered by fractionation. The hard resin in this instance is not polymerised. Properties of so separated hard resins are being studied.

#### 190. Possibility of production of nicotine and its salts from tobacco waste in the Bombay Presidency.

V. C. AMIN and M. S. PATEL, Bombay.

Large quantities of tobacco waste are available in tobacco producing districts of the Bombay Presidency, especially in the District of Belgaum. It is estimated that about 200 to 300 tons of tobacco waste are available



in that district alone. A process for commercial production of nicotine suitable to local conditions has been worked out. It has been found that it is possible to prepare crude nicotine and nicotine sulphate at a very reasonable cost. The product has been found satisfactory by some of the importers of nicotine and nicotine products in the United Kingdom. In the beginning a large portion of the production will have to be exported and only a part can be utilized in this country. As the use of nicotine and nicotine salts for insecticidal purposes becomes popular in this country it is hoped that all the production of the proposed plant treating about  $\frac{1}{2}$  ton of tobacco waste per day would be consumed locally.

Fatty acid salts of nicotine such as nicotine stearate, oleate and nicotine salts of fatty acids from groundnut oil, linseed oil and castor oil have been prepared. Their physical, chemical and bactericidal properties have been studied.

### 191. Low temperature distillation of coal and heavy tar.

K. L. RAY, B. C. GUHA, and H. K. SEN, Calcutta.

Recent investigations show that the distillation of coal and tar oil mixtures considerably increases the yield of light oil (*Industrial and Engineering Chem.*, June 1936), but as yet no commercial plants for this have been constructed. In all these samples of coal, the percentage of ash is substantially lower than that of an average second class Indian coal. The present work has for its object the caking of non-coking coals, and a study of the volatile products of coal-tar oil distillation under low temperature conditions. The yield of tar, after deducting the probable contribution of the added tar, is found in most cases to be between 65 and 75 gallons per ton of coal of which the ash content is between 17 and 19%. The tar when fractionated, yields :

11 gallons of light oil boiling up to 170°C.

35.8 „ „ middle „ „ „ 230°C.

24 „ „ heavy „ „ „ 360°C.

Pitch – approximately 11% of the weight of tar.

The gas analysed :

CO<sub>2</sub>, 2.8% ; O<sub>2</sub> nil ; C<sub>2</sub>H<sub>4</sub> 4.0% ; CO, 6.5% ; H<sub>2</sub>, 39.3% ;

CH<sub>4</sub>, 43.0% ; N<sub>2</sub>, 4.4%.

### 192. The destructive distillation of groundnut shells.

G. RAMA RAO, Hyderabad (Deccan).

Groundnut shells are obtainable in abundance in the Hyderabad State. This work was undertaken to examine the suitability of commercial production of methyl alcohol, acetic acid and combustible gases from these. The thermal decomposition has been studied with special reference to the rate of evolution of the gases, their volumetric composition and calorific value. It has been found that the volume of combustible gases is more and has a higher calorific value than that obtained in the dry distillation of wood. The yields of acetic acid and methyl alcohol in the pyrolygenous acid compare favourably with those from the dry distillation of wood besides containing some ammonia.

### 193. Carbonization assays of Indian coals.

M. R. MANDLEKAR, Bangalore.

With a view to ascertain the different properties of coals which would determine the suitability of the material for special industries, e.g. glass manufacture, metallurgical operations, gas industry, etc. an investigation into the carbonization assays of Indian coals has been commenced.



## 194. Gas making from cheaper grades of fuel oils.

G. RAMA RAO, Hyderabad (Deccan).

This paper deals with the cracking of Borneo Diesel oil and crude oil in a Mansfield gas producer. The rate of evolution of the gas, the rate of consumption of oil and the calorific value of the gas have been studied. The tar has been fractionated with a view to find useful products.

## 195. The cleaning of power station flue gases with particular application to Hyderabad State power station.

W. E. J. BEECHING, Hyderabad (Deccan).

Of the many systems for cleaning power station gases, the best known are the dry and the wet systems. The former consists of cyclones cleaning by centrifugal force, and electrostatic precipitators which pass the gases through an electrostatic field between two sets of electrodes. The wet systems involve water films, water sprays or a combination of both; these remove the dust, and also dissolve the sulphur.

Hyderabad power station has a pulverized fuel firing which rules out dry cleaning. A standard wet system, involving considerable structural alterations would have been very costly. Investigations made to find a cheaper solution showed that in the presence of coke the water required was much less for the absorption of  $\text{SO}_2$ . Highly aerated wash water, preferably above  $160^\circ\text{F}$ . the presence of manganese, or iron as catalysts oxidizes the  $\text{SO}_2$  to the highly soluble  $\text{SO}_3$ .

An experimental plant of two interconnected large cylinders, both fitted with water sprays, and shelves of coke in the second, was constructed; practically all the dirt was removed, and acid trickled down the inside of the second cylinder.

The acidic effluent can be suitably treated to obtain either calcium bisulphite for paper mill requirements or sodium sulphite for the wood pulp industry.

### Bio-chemistry

## 196. The synthesis of vitamin C by germinating seeds.

B. N. GHOSH and B. C. GUHA, Calcutta.

Germinating *kanchamung*, *mator*, *barboti*, *chhola* have been investigated in relation to their power to synthesize vitamin C from mannose at different hydrogen ion concentrations. There are very great differences in the behaviour of the different seeds in this respect.

## 197. On ascorbigen.

B. C. GUHA and J. C. PAL, Calcutta.

Practically conclusive evidence has been obtained to show that part of the ascorbic acid present in many vegetable foodstuffs is present in a combined form, from which the free vitamin can be released by heating with water. This combined ascorbic acid has been called 'ascorbigen'. It has been possible to extract ascorbigen from cabbage free from ascorbic acid. Further investigations are proceeding as to its isolation and properties.

## 198. Some properties of ascorbigen.

P. N. SEN GUPTA and B. C. GUHA, Calcutta.

Working with cabbage, various solvents have been tried for extracting ascorbigen free from ascorbic acid. Processes have been discovered by which a considerable concentration of ascorbigen has been effected.



199. The distribution of ascorbic acid oxides in plant and animal tissues.

R. K. CHAKRABORTY and B. C. GUHA, Calcutta.

In an attempt to study the properties of the enzyme, ascorbic acid oxidase, a preliminary survey has been made of the oxidase content of many plant animal tissues. In general, the animal tissues investigated including the liver and kidney tissues of the cow, guinea-pig, rabbit, fish and fowl, appear to contain practically no ascorbic acid oxidase. Among the vegetable food-stuffs studied, sasha (cucumber) appears to be the richest source of the enzyme, while many common Indian fruits like pineapple, mango, guava, etc. seem to be practically free from it.

200. The nature of sweet potato amylase.

K. V. GIRI, Bangalore.

Sweet potato amylase behaves like a pure  $\beta$ -amylase in the hydrolysis of amylo-amylase. The amylase hydrolyses a portion of starch, leaving a residual material which gives violet colour with iodine. This residual material is hydrolysed by  $\beta$ -amylase with great difficulty, while the  $\alpha$ -amylase of malt hydrolyses it in such a way that the colouration with iodine disappears at a low maltose level. The hydrolysis of amylo-amylase by sweet potato amylase is followed by decrease in the intensity of blue colour, thereby showing that  $\beta$ -amylase attacks those groups in the starch molecule which are responsible for the blue colour with iodine. The bearing of these results on the recent developments in the constitution of starch is discussed in detail.

201. Magnesium activation of tissue phosphatases.

K. V. GIRI and N. C. DATTA, Bangalore.

The susceptibility of the phosphatases of liver, kidney brain and bone to activation by magnesium has been studied in detail in relation to their purity, method of preparation and age. The results indicate that the degree of activation is very much enhanced on ultrafiltration. In some cases it was found that the phosphate of the crude extracts was not activated by magnesium, while the same extracts on ultrafiltration were found to respond to magnesium activation to a considerable degree. It is concluded from the results that the susceptibility to activation by magnesium depends on the complexity of the enzyme colloid, and the presence of concomitant substances present in the extract. A method of determining the true value of the phosphatase activity in tissues has been suggested.

202. Plant phosphatases.

K. V. GIRI, Bangalore.

*The phosphatase from sprouted soya bean.* A highly active preparation of phosphatase from sprouted soya bean has been obtained by purification of the crude aqueous extracts of the germinated seed powder. The method consists of (a) fractional precipitation with alcohol or acetone, (b) solution of the most highly active fraction, (c) precipitation of the impurities at pH 5.0, and (d) final dialysis or ultrafiltration. A very active preparation was obtained, whose activity was about 102 Ph.P.E./mg. For glycerophosphate hydrolysis and about 210 Ph.P.E./mg. for pyrophosphate hydrolysis. The preparation is about 350 times as active as that of the original sprouted seed powder. It gives protein and carbohydrate reactions. The behaviour of the purified enzyme under different conditions of temperature, pH, its specificity towards various phosphoric



esters and its activity in presence of various salts has been studied in detail. The relation between the activity of the phosphatase and vitamin C in association with metals like Cu has also been studied.

*Soluble and insoluble phosphatases in cereals.* In continuation of previous work (*Proc. Ind. Sci. Cong.*, 1936, p. 57) the state of phosphatases occurring in seeds and their changes during the germination of seeds has been further investigated. It has been found that in soya bean the phosphatase is partly soluble and can be extracted with water. On treatment with acetone and ether in order to remove the fat, the adsorbed phosphatase is rendered soluble, thereby showing that a part of the enzyme is probably adsorbed to the fat contained in the seed, which renders it insoluble. Similar studies have been made with other cereals, and it is suggested that in oil seeds, protein rich seeds and starch containing seeds, the enzyme is partly adsorbed to the fat, protein and starch respectively, and that different methods of extraction have to be tried, depending on the nature of the seed, in order to bring the phosphatase into a soluble and active state.

*Glycero- and pyrophosphatase systems in plants and animal tissues.* From a study of several plant materials and animal tissues it has been found that the ratio :—

pyrophosphate P : glycerophosphate P

is greater than 1 in the case of plant extracts and less than 1 in the case of animal tissues, when the enzyme is allowed to act on the respective substrates and the inorganic P liberated is determined. This difference in the properties of the phosphatase systems of plants and animals may be applied to cases where the origin of the phosphatase has to be determined.

### 203. A micro method for the determination of phosphatase activity in biological fluids.

V. RANGANATHAN, Bangalore.

The release of inorganic phosphate from glycerophosphate when it is hydrolysed by phosphatase can be measured by the increase in conductivity of the solution. This property has been applied to the determination of the activity of phosphatases in blood and other tissues under standard conditions of temperature and pH. It has been found that this affords a very convenient method for measuring the changes in the activity of the phosphatase in blood, which sometimes varies with the different types of disease. The method is considered, therefore, to be of value in the diagnosis of diseases like rickets which affect the phosphatase activity of blood. By this method very small quantities such as  $10^{-2}$  milligrammes of phosphorus can be very accurately determined. Further work is in progress in this direction.

### 204. The amylase system of rice grain during ripening and germination.

K. VENKATA GIRI and A. SREENIVASAN, Bangalore.

In the resting rice grain a large part of the amylase is in an adsorbed condition and is therefore not extracted with water. Phosphate buffer extraction at pH 7 produces a considerable increase in the amylolytic power of the rice grain, both in the saccharifying and in the dextrinising functions. Resting rice grain contains two amylases with different pH optima. The amylase of optimum pH 4.6 behaves like pure  $\beta$ -amylase, while that of optimum pH 7 behaves like pure  $\alpha$ -amylase in their hydrolysis of amyloamylose. The two amylases are present in a highly active state in the rice grain at milk stage, but become gradually inactive with the advance in ripening until in the fully ripened grain, they exist in such a condition that they cannot be extracted with water. During germination on the other hand, the amylases increase in activity. The



pure  $\alpha$  and  $\beta$  amylases of resting rice grains are each converted into an amylase system ( $\alpha + \beta$ ) characteristic of malt on germination.

During the ripening of the rice grain, the activity of the phosphatase decreases with the advance in ripening. There is also a corresponding decrease in the inorganic phosphate content of the grain and increase in the phytin phosphorus. During germination the reverse of the above happens, viz. an increase in the activity of the phosphatase and in the inorganic phosphorus and a decrease in the organic phosphorus. It is suggested that the phosphate formed as a result of phytin hydrolysis during germination serves to elute the amylases which are otherwise present in a dormant condition and thus render them active.

The bearing of the results on the problem of amylolytic changes during the ripening and germination of cereals is discussed. Work relating to the distribution of the two amylases in the different parts of the rice grain and their changes during the storage of freshly harvested paddy is in progress. This work is being extended to other cereals as well.

## 205. Extraction and chemical analysis of the proteins of green gram and lentil.

K. P. BASU, M. C. NATH, and M. O. GHANI, Dacca.

Green gram (*Phaseolus Mungo*) and lentil (*Lens Esculenta*) have got almost the same percentage composition (protein content of the first being 23.20% and that of the latter 22.60%).

Percentage of total nitrogen extractible by different solvents in both cases is 92.3.

In case of green gram the maximum amount of protein is extracted by 3% salt solution while 2.5% salt is the best concentration for lentil.

As many as seven different proteins have been isolated from green gram, but only three in case of lentil. It was not possible to obtain the water soluble protein of lentil, in pure condition.

Elementary composition of the isolated proteins have been found by microanalysis and nitrogen distribution of the proteins (as different amino acids) has been made by the method of Van Slyke as modified by Plimmer and Rosedale.

Proteins in lentil are markedly deficient in cystine, which might account for the lower biological values obtained with this pulse and also might easily explain the loss of fur, observed in the long period feeding experiments.

Lentil contains a smaller percentage of histidine (an essential amino acid) than the green gram; but both arginine and lysine contents of lentil are higher than those of green gram.

Auto-hydrolysis of proteins in lentil is less than those in green gram and is therefore not the cause of the presence of such a large amount of non-protein nitrogen in the former.

## 206. Extraction and chemical analysis of proteins of *Lathyrus Sativus*.

K. P. BASU and R. MUKHERJEE, Dacca.

Water extracts 45.2%, sodium chloride 36.2%, alcohol 1.2% and 0.2% alkali 11% of the total proteins of *Lathyrus Sativus*. The proteins have been analysed by the Van Slyke method and tyrosine, tryptophane and cystin have been estimated colorimetrically. The proteins appear to be deficient in tryptophane. Daily addition of tryptophane to young rats on *Lathyrus Sativus* diet restored the healthy appearance of rats and silkiness and smoothness of fur but no enhancement of growth was observed.



207. Extraction and chemical analysis of proteins of aus and aman rice.

K. P. BASU and M. N. BASAK, Dacca.

1. From aman rice (Bhashamanik), water extracts 5.8%; salt 22.6%; 75% alcohol 3.7%; and alkali 62.7% of the proteins; the corresponding values for aus rice are 7.5%, 29.2%, 3.0% and 55.7% respectively.

2. Aus and aman rice globulin and glutelin have been extracted and analysed by the Van Slyke method. Tyrosine and tryptophane contents of these proteins were determined by colorimetric method.

3. Aman rice contains more sulphur containing amino-acid and more arginine than aus rice.

4. Additions of either cystine or methionine in equivalent amounts cause growth in rats on aus rice diet (protein content 5%), which in its absence is incapable of promoting any growth. It is suggested that the sulphur containing amino acid requirement for growth is higher than that for maintenance.

208. Determination of nitrogen in pulses.

A. SREENIVASAN and V. SADASIVAN, Bangalore.

In the determination of total nitrogen in pulses (like *Glycine hispida*, *Pisum sativum*, *Cicer arietinum*, *Phaseolus mungo* *Dolichos lablab*, etc.) by the Kjeldhal method, it has been observed that highly inconsistent and usually low values are obtained when the digestion is stopped soon after the mixture begins to clear. Accurate and concordant results are obtained only when the digestion is continued for some time after the stage of clearance. Soaking with water prior to commencement of digestion considerably hastens the progress of digestion and often in such cases correct values are obtained when the digestion is stopped soon after the mixture clears. Germinated pulses digest also quicker and correct values are obtained in such cases by 'dry' digestion with sulphuric acid even when the digestion is stopped at clearance stage. It is suggested that germination or boiling with dilute sulphuric acid results in a partial breakdown of the protein compounds into more easily decomposable substances.

With peas, however, the germinated seeds give higher values for total nitrogen than the ungerminated ones. Work is in progress to determine whether or not this increased nitrogen content of germinated pea seeds is due to any nitrogen fixation.

209. Detection of adulteration of cereal flours by the 'agar plate' method.

P. N. BHARGAVA and K. VENKATA GIRI, Bangalore.

The method (*Science*, 1935, 81, 343) previously developed for the differentiation of pure starches, has been extended for the differentiation of cereal flours, and their detection when present in mixtures. The cereal flours have been classified into groups according to their characteristic coloured diffusion zones developed when a drop of amylase solution has been allowed to diffuse through an agar plate impregnated with the boiled extract of the flour, and finally flooded with iodine. The method has been successfully applied to the detection of rice flour in wheat flour. It has been found possible to judge easily to the nearest 20 per cent. of rice in a given mixture. The method has also been applied to the detection of adulteration of rice with maize; admixture of ragi with wheat or maize, barley with wheat, jowar with rice, etc. The method is particularly



useful when the material is cooked, in which case there is no method available for the detection of adulteration.

## Discussions

### 210. On the use of some new reagents in macro- and micro-analysis.

P. RAY, Calcutta.

Within the last few years we have studied some organic compounds for use as analytical reagents, and three of these have been found very useful. These are rubeanic acid, quinaldinic acid and dimercapto-thiobiazole.

*Rubeanic acid or dithio-oxamide*, which may exist in a tautomeric thiol form, reacts with copper, nickel and cobalt ion to give intensely coloured insoluble precipitates. The substance has been placed on the market as reagent for the above metals. As the colour of the precipitate differs for different metals, the reagent can be employed to detect these metals in presence of one another by means of spot tests. It has also been employed for the detection of ruthenium, palladium and platinum (Wolbling and Steiger, *Mikrochem.*, 15, 295, 1934).

The colour of the precipitate given by different metals with rubeanic acid is as follows:—Copper-greenish black, nickel-blue, cobalt-brown, ruthenium-blue, palladium-fire-red, platinum-brownish red.

*Quinaldinic acid or quinoline-carboxylic acid* gives a quantitative precipitation of copper from mineral acid solution, of cadmium and ferrous iron from neutral solution, and of zinc from acetic acid and slightly ammoniacal solution.

The acid has been utilized with excellent results for the estimation of copper in the presence of all other metals excepting zinc. The presence of even phosphoric and arsenic acids does not interfere.

Equally good results have been obtained in the estimation of zinc in acetic acid solution whereby it can be separated from manganese, phosphoric acid, arsenic acid, calcium, strontium, barium, magnesium and alkali metals. In ammoniacal solution containing tartaric acid, zinc can be estimated with this reagent in presence of iron, aluminium, uranium, beryllium and titanium.

Cadmium has also been estimated as cadmium quinaldinate in neutral solution.

Colorimetric estimation of Fe ion has also been effected with the reagent with good results. A violet colour is developed in presence of traces of ferrous iron.

The precipitates of copper, zinc and cadmium can be directly weighed.

The reagent has been used with quite satisfactory results for the micro-estimation of copper and zinc.

*Dimercapto-thiobiazole* has been found to give coloured precipitates with most of the metals of the second analytical group. Of these the copper compound is most insoluble. Bismuth and lead compounds come next in order.

Copper can be separated in mineral acid solution, or under suitable conditions, from As, Sb, Sn, Mo, W, Fe, Zn and all metals of the group three (analytical) and the succeeding ones.

Lead has been separated from As, Sb, Sn, Mo and alkaline earths in presence of tartaric acid and alkali fluoride.

Bismuth gives a bright scarlet-red precipitate, which is highly characteristic. It can be used as a very sensitive test for the micro-detection of bismuth in presence of all other metals except copper. The interfering action of lead, arsenic, antimony, tin and mercury can be eliminated by the addition of alkali fluoride. This reaction with bismuth was also studied by Dubsky and Okac (*Zeit anal. Chem.*, 96, 267, 1934).

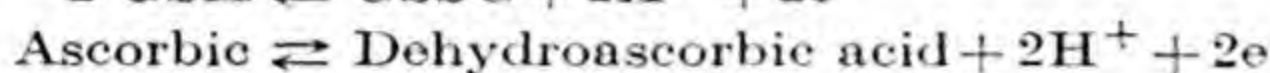


The dithiol precipitates cannot be weighed directly, and hence the reagent is used for the purpose of separation only.

## 211. Oxidation-reduction potential of sulphhydryl bodies, ascorbic acid and other systems of biological interest.

J. C. GHOSH and T. L. RAMACHAR, Dacca.

Oxidation-reduction processes are now interpreted in terms of electron transfer, and the free energy of such migration can be expressed in terms of electrode-potentials. If the oxidation or rather dehydrogenation of glutathione and ascorbic acid are reversible processes, as given by the equations below



the electrode potentials of these systems on an inert metal surface should be given respectively by the equations

$$E_h = E_0 - \frac{RT}{F} P_H + \frac{RT}{F} \log \frac{[\sqrt{\text{GSSG}}]}{[\text{GSH}]} \text{ for glutathione system} \dots\dots (1)$$

and

$$E_h = E_0 - \frac{RT}{F} P_H + \frac{RT}{2F} \log \frac{[\text{Dehydroascorbic acid}]}{[\text{Ascorbic acid}]} \dots\dots\dots (2)$$

Dixon and Quastel, Michaelis, Flexner, Barron etc. following ordinary procedure found that the potential of sulphhydryl compounds is given by the empirical equation :

$$E_h = E_0 - \frac{RT}{F} P_H + \frac{RT}{F} \log \frac{1}{[\text{GSH}]}$$

and for ascorbic acid Green found that the potential is still less susceptible to thermodynamic treatment and is expressed by the equation :

$$E_h = +.375 - .060 P_H$$

The cause of these anomalous behaviour has been traced to the film of oxygen or oxide which is present on even noble metal surfaces and which in the case of mercury cannot be removed by long continued evacuation. A new experimental technique has been developed according to which this oxygen film tenaciously adhering to the surface of electrode metals was removed by cathodic discharge of hydrogen, which simultaneously reduced the oxidant present in the solution bathing the electrode. After electrolysis a stream of pure nitrogen was bubbled through the solution for a few hours and the steady value of the potential of the electrode, which functioned as a cathode during electrolysis, was measured. The electrode potentials have been found to be in agreement with the thermodynamic equations (1) and (2). Investigations on the electrode potential of lactic-pyruvic acid systems by means of the above technique are in progress.

## 212. Initiation of chemical reactivity under electrical stimulation.

S. S. JOSHI, Benares.

Data are given for a chemical change in  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{Cl}_2$ , benzene, wax paraffins,  $\text{H}_2\text{S}$ ,  $\text{CaCl}_2$  both when pure, and in the presence of foreign gases and different electrical and working conditions. A review of work on the kinetics of chemical change under different types of electrical discharges, exposure to  $\alpha$ -rays, short wave and heat radiations has been made with a view to obtain points of contact and similarity of mechanism. A theory for the velocity of the chemical reactions under the electrical discharge has been developed



on the basis of the fractional time of a period characteristic of a given A.C. supply. The after-effects of this electrical activation proceed markedly differently from those observed, especially in thermal activation. Reaction chains are set up along the trajectory of the moving ion, for which a quantitative explanation is given on the basis of the above theory (cf. also Elliott, Joshi and Lunt, *Trans. Farad. Soc.*, 1927, 23, 57). Furthermore, the course of a change produced electrically may be more complex than its thermal or photochemical analogue. Determination of the ionization current flowing through the reaction space has been found to be a sensitive indicator of the course of the reaction, even where the change involved is only physical or quasi-chemical. Wall catalysis has been found to be an appreciable factor in the electrical as in other types of activation. An observation has been made, capable of wide application, that the conditions characteristic of the occurrence of a chemical change by electrical activation are best explored by means of a quantity designated the 'threshold potential', which resembles, but is different from the Paschen potential. In terms of this, it is possible to investigate a variety of catalytic and allied influences on the initial atom and the mechanism of the 'main' reaction. An evaluation of this quantity, not studied quantitatively hitherto in the literature of the subject, has been found to be of much utility in explaining the observed variations in the current, dissipation of energy in the system, the power factor and the fractional voltage on the reaction space during the progress of a given reaction.

### 213. The alkaloids of *Holarrhena antidysenterica*.

S. SIDDIQUI, Delhi.

After a brief reference to the history and uses of *Holarrhena antidysenterica* and the work done on its alkaloids from 1858 to 1930, the paper would deal in detail with the entire work on the subject carried out since, by me and my co-workers. This work extends in two directions:

1. The isolation of eight subsidiary alkaloids of conessine and the fixing up of their interrelationship, chiefly through the methylation of some of them to conessine and the N-demethylation of conessine to two of its subsidiary bases. In this connection, would also be discussed the claims of several other alkaloids, isolated by various authors (Ghosh and Bose, *Archiv. and Pharm.*, 1932, 270, 100; Haworth, *J.* 1932, 631; Bertho, Schueckmann and Schonberger, *Ber.*, 66, 786, 1932; Peacock and Chaudhri, *J.* 1935, 734) during this period, to be considered as uniform products.

2. Studies in the conessine series, involving its isomerization and oxidation and also the investigation into the relationship between the comparative N-stability of conessine and *iso*-conessine on the one hand and their respective pharmacological activity on the other.

Most of the work outlined above has already appeared in eight publications (*J. Ind. Chem. Soc.*, 1932, 553; 1933, 673; 1934, 283; 786; *Proc. Ind. Acad. Sci.*, 1935, A, 2-426; 1936, A, 3-249; 1936, A, 3-257; 1936; 1936, 3. A.). Some of it however is still unpublished and this includes the degradation of conessine and *iso*-conessine to a common hydrocarbon indicating the nature of relationship between the two bases.

The paper would also deal with the improved methods of isolating the chief alkaloid, conessine, with a view to its industrial exploitation.

### 214. Nitrogen transformations in the soil.

N. R. DHAR, S. K. MUKERJI, E. V. SESHACHARYULU, and S. P. TANDON, Allahabad.

Nitrogen fixation by the addition of molasses to soil in fields.

Nitrogen fixation in the induced and catalytic oxidation of glucose or canesugar.



- Nitrogen fixation in the oxidation of molasses mixed with soil.
- Azotobacter fixes nitrogen very well in Tropical soils.
- Composts made with molasses when added to soil in heaps.
- Nitrogen fixation in the photo-oxidation of canesugar mixed with sterilized soil in quartz vessels.
- Nitrogen fixation and azotobacter count on the application of molasses, carbohydrates, starch and glycerol to soil.
- The probable mechanism of nitrogen fixation.
- No denitrification takes place on the addition of molasses to fields.
- Fixation of nitrogen in the oxidation of cellulosic substances mixed with soil.
- Nitrogen fixation in the oxidation of sodium salts of organic acids.
- Influence of light on nitrification and ammonification.
- Photo-oxidation of nitrite to nitrate.
- Influence of temperature on the bacterial nitrification.
- Influence of temperature on the ammonification of urea.
- Influence of temperature on the nitrogen fixation by Azotobacter.
- Available nitrogen in Tropical soils.
- Significance of carbon-nitrogen ratio in soil.
- Influence of temperature on the carbon-nitrogen ratio in soils.
- Loss of nitrogen from soils and its retardation.
- Decomposition of solutions of ammonium nitrite.
- Decomposition of mixture of ammonium sulphate and potassium nitrite mixed with dry soil.
- Nitrogen loss from mixtures of alanine and potassium nitrite mixed with soil.
- Nitrogen loss by exposing to sunlight ammonium salt and nitrite solution mixed with soil under sterile condition.
- Part played by organic manures.
- Influence of sunlight in the nitrification and denitrification of ammonium sulphate added to fields.
- Retardation of nitrogen loss from field soils by the addition of molasses.
- Molasses and press mud in reclamation of alkali land.
- Vast tracts of land in India are alkaline.
- Defects of alkali lands.

## 215. The detection and estimation of degradation in cotton.

R. B. FORSTER and K. VENKATARAMAN, Bombay.

Following a brief review of the physical and chemical evidence on which the accepted structure of cellulose is based, its implications in textile processing are discussed. The objective of the bleacher is to produce as near an approximation to 'standard' cellulose as possible; deviations from this ideal may be followed quantitatively by determinations of (a) the moisture content, (b) the ash and ash alkalinity, (c) reducing power ('copper number'), (d) fluidity in cuprammonium solution, (e) absorption of methylene blue, and (f) strength tests. The moisture content may be conveniently estimated by distilling the cotton with xylene or dioxane, leading the distillate into acetic anhydride and analysing the acetic acid-anhydride mixture. A rapid method for determining the reducing power, which may also give an insight into the nature of the degradation, is to extract the cotton with standard caustic soda solution, neutralize with standard acid and titrate with ceric sulphate solution. The affinity of oxycellulose for metallic ions at present provides the only method available for differentiating it from hydrocellulose, i.e. for distinguishing excessive bleaching from excessive souring. A more satisfactory test and a method of estimating the relationship of the reducing power of a sample of cotton to its aldehydic and carboxylic contents are desirable. Preliminary experiments in this direction are described.



## Symposium.

216. The teaching of applied chemistry in Indian Universities.

J. N. RAY, Lahore, will preside.

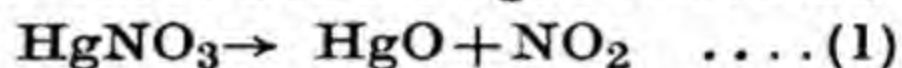
DR. R. B. FORSTER, Bombay ; K. G. NAIK, Baroda ; DR. K. VENKATARAMAN, Bombay ; DR. H. K. SEN, Ranchi ; DR. SRIKANTAN, Waltair and others are expected to speak.

217. Thermal decomposition of mercurous nitrate.

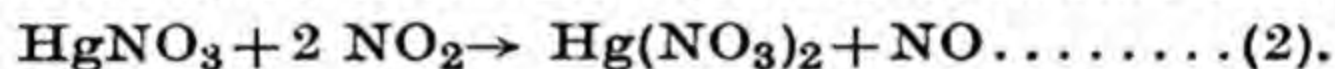
M. S. SHAH and B. G. JOSHI, Ahmedabad.

In continuation of the previous work (*Proc. Ind. Sci. Cong.*, 1935 P. 174), the authors have studied the decomposition of mercurous nitrate in detail by heating the substance in vacuo at various temperatures and analysing quantitatively the solid and gaseous products of the decomposition. Two series of experiments were performed : in the first series, the gaseous products were removed by evacuating the system at the temperature of experiment, while in the other series, evacuation was carried out at room temperature after allowing the gaseous products to be absorbed by the solid product of the decomposition for a period of 12 hours.

The results of the above experiments together with the observations recorded before (*loc. cit.*) show that mercurous nitrate decomposes primarily into mercuric oxide and nitrogen tetroxide, as



Some nitrogen tetroxide produced in (1) oxidises undecomposed mercurous nitrate to mercuric nitrate with the evolution of nitric oxide, as



The mercuric nitrate so formed in (2) undergoes decomposition above  $200^\circ$  as shown in the following abstract, the ultimate product of decomposition being a scarlet red oxide of mercury.

When the gaseous products of the decomposition are allowed to be absorbed at room temperature by the solid product of decomposition, nitric oxide is left unabsorbed in the gaseous state while nitrogen tetroxide is absorbed by mercuric oxide, probably with the formation of mercuric nitrite and mercuric nitrate.

218. Thermal decomposition of mercuric nitrate.

M. S. SHAH and B. G. JOSHI, Ahmedabad.

The decomposition of mercuric nitrate has been studied by heating the substance in vacuo at  $100^\circ$ ,  $150^\circ$ ,  $200^\circ$  ...  $300^\circ$ , and examining the solid and gaseous products of the decomposition.

The decomposition which is very slow at  $100^\circ$ , becomes rapid above  $200^\circ$  and is practically over at about  $300^\circ$ , and can be represented as



219. Interaction between mercury and nitrogen tetroxide : Isolation of nitro-mercury.

M. S. SHAH and B. G. JOSHI, Ahmedabad.

The action of (i) gaseous and (ii) liquid nitrogen tetroxide on mercury has been studied by conducting experiments with varying amounts of mercury and nitrogen tetroxide in vacuo at  $25^\circ$  and  $-8^\circ$  respectively and analysing the solid and gaseous products of the interaction at room temperature. In both cases, the reaction starts with the evolution of nitric oxide and the formation of greyish black substance. With



liquid nitrogen tetroxide, the reaction is rapid and the greyish black substance is immediately converted into mercurous nitrate, whereas with gaseous nitrogen tetroxide, the reaction being slow, the formation of mercurous nitrate is observed only on its surface.

If by constant shaking a fresh surface of mercury were exposed to nitrogen tetroxide vapours, the formation of mercurous nitrate is reduced to a minimum, and the greyish black substance is obtained in quantity. This substance on examination is found to be nitro-mercury : a complex containing mercury, mercurous oxide and some adsorbed nitrogen tetroxide.

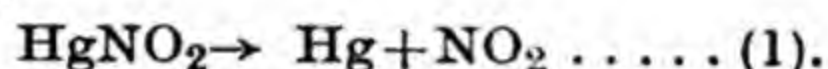
## 220. Thermal decomposition of mercurous nitrite.

M. S. SHAH and B. G. JOSHI, Ahmedabad.

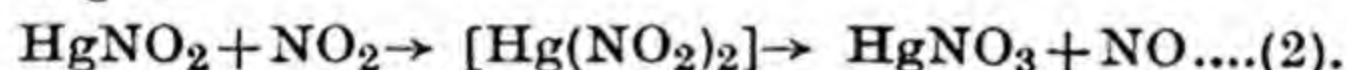
The decomposition of mercurous nitrite has been studied in detail by heating the substance in vacuo at various temperatures and analysing quantitatively the sublimate and the solid and gaseous products of decomposition at the end of each experiment. The decomposition which starts in the neighbourhood of  $125^{\circ}$ , becomes rapid when the temperature is raised, and comes to an end at about  $300^{\circ}$ .

The observations collected in the above experiments together with other facts noted in experiments on (i) the action of nitrogen tetroxide on mercurous nitrite at  $100^{\circ}$ , (ii) the interaction between mercury and nitrogen tetroxide at  $200^{\circ}$ , and (iii) the decomposition of mercurous nitrate above  $100^{\circ}$ , show that the probable mechanism involved is as follows :—

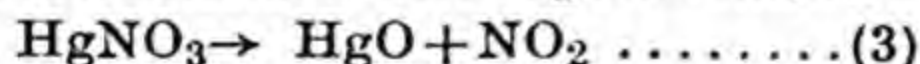
A part of mercurous nitrite decomposes initially into mercury and nitrogen tetroxide, as



In the second stage, nitrogen tetroxide produced in (1) reacts slowly with mercury as shown in the preceding abstract, and rapidly with undecomposed mercurous nitrite giving mercurous nitrate and nitric oxide according to



The mercurous nitrate so formed undergoes decomposition simultaneously under the conditions of the experiment, as



and the nitrogen tetroxide produced in (3) helps further conversion of mercury and mercurous nitrite into mercurous nitrate as shown above.

When all mercurous nitrite has thus undergone a change, the decomposition corresponds to that of mercurous nitrate.



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# Indian Science Congress Association

Twenty-fourth Year

1st February, 1936—31st January, 1937

Notices. Rules.

Lists of Officers and Members.

ROYAL ASIATIC SOCIETY OF BENGAL

1, Park Street  
CALCUTTA

July, 1936







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July, 1936







## TWENTY FOURTH ANNUAL CONGRESS

The Twenty-fourth Annual Meeting of the Indian Science Congress will be held in Hyderabad (Deccan) from January 2nd to 8th, 1937.

His Exalted Highness, Rustom-i-Dowran, Arastu-i-Zaman, Lt.-General Muzaffarul-Mulk Wal-Mamalik, Nawab Sir Mir Osman Ali Khan Bahadur, Fateh Jung Sipah Salar, Faithful Ally of the British Government, Nizamud-Doula, Nizam-ul-Mulk Asaf Jah, G.C.S.I., G.B.E., Nizam of Hyderabad, has consented to be the Patron of the Meeting.

Rao Bahadur T. S. Venkataraman, B.A., I.A.S., Imperial Sugarcane Specialist, Lawley Road, Coimbatore, South India, will be the President.

Ordinary Members intending to read papers should forward them together with three copies of an abstract so as to reach the President of the Section concerned not later than the 15th September, 1936, for submission to the Sectional Committee. Abstracts should be typewritten and must not exceed 200 words. They should not include formulæ or diagrams.

The enclosed form should be filled in and attached to the papers sent. A model is attached in case duplicates are needed.

The names and addresses of the Sectional Presidents are given in the list of Officers.

Papers submitted for reading at the Session of the Congress can only be submitted direct by Ordinary and Full Session Members, and by Associate Session and Student Session Members only through Ordinary Members.

All enquiries as to accommodation should be addressed to the Local Secretaries whose names and addresses are given in the list of Officers. It is particularly requested that very early intimation of the accommodation required should be sent to the Local Secretaries.

Ordinary Membership cards have been forwarded to all Ordinary Members.

A detailed programme of the Twenty-fourth Meeting of the Congress will be issued to all Ordinary Members in the course of December of this year, together with the usual abstracts of papers accepted for reading in the Sections.

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## TWENTY-FIFTH ANNUAL CONGRESS, 1938

Subscription bills will be sent out to all Ordinary Members on the register after the 1st of February, 1937. These will be followed, after a suitable interval, by the Ordinary Membership



cards for the year 1937-38 which will be issued per V-P.P. to the amount of the subscription. Only payment of the subscription fee of Rs. 10 before the 15th July, 1937, will be effective for continuance of Ordinary Membership during the ensuing year, covering the Twenty-fifth Annual Congress.

Application forms for Ordinary Membership may be at any time obtained from the office of the Royal Asiatic Society of Bengal, 1, Park Street, Calcutta.

A list of Ordinary Members of the Association will be issued to all Ordinary Members after the 15th July, 1937, together with all necessary information.



## RULES

### INDIAN SCIENCE CONGRESS ASSOCIATION

1. The name of the Association shall be the Indian Science Congress Association, and its object shall be the advancement of Science in India by the annual holding of a Congress and the doing of all such things as are incidental or conducive to the above object, including :—

- (a) the holding and management of funds and property ;
- (b) the acquisition of rights and privileges necessary or convenient for the object of the Association ;
- (c) the management, development, improvement, disposal, and sale of all and any parts of the property of the Association.

2. The Association shall consist of Ordinary Members and Session Members.

3. Ordinary Members of the Association shall have the right to contribute papers for reading at the Session of the Congress, to receive free of charge all publications issued by the Association, and to fill any office in the Association on being duly elected thereto.

4. The annual subscription of Ordinary Members shall be Rs. 10. The subscription shall become due on the 1st February of each year, and shall only be effective as a payment for Ordinary membership subscription if received before the 15th July of the year.

5. Any Ordinary Member may compound for the payment of all future annual subscriptions by the payment in a single sum of Rs. 150.

6. There shall be three classes of Session Members :—

- (a) Full Session Members—Subscription Rs. 10 per Session.
- (b) Associate Session Members—Subscription Rs. 5 per Session.
- (c) Student Session Members—Subscription Rs. 2 per Session.

7. Full Session Members shall have the right to contribute papers for reading at the Session of the Congress, and to receive free of charge all publications issued by the Association relating to the Session of the Congress of which they are Members.

Associate and Student Session Members shall have the right to submit papers for reading at the Session of the Congress of which they are Members provided such papers be communicated through an Ordinary Member of the Association.

A Student Member shall before admission be duly certified by the head of his Institution to be a *bona fide* student.

8. The official year of the Association shall commence from the 1st of February.

9. There shall be Officers of the Association consisting of the Members of the Executive Committee and Presidents and Recorders of Sections.

10. Only Ordinary Members shall hold office in the Association.

11. The term of office of all Officers of the Association except the President shall commence from the beginning of the official year and shall extend until the assumption of office by their successors appointed in accordance with the provisions of these Rules. The President shall



assume office on the opening day of the Annual Congress following the one at which he is appointed, and shall continue to hold office until the assumption of office by his successor.

12. There shall be an Executive Committee which shall carry on the administrative work of the Association and submit such questions as it thinks desirable to a General Committee at its Annual Meeting during the Session of the Congress or at a Special Meeting of which due notice shall have been given.

13. The Executive Committee shall consist of the President, the President-elect for the following year, the two General Secretaries, the Treasurer (who shall be the Treasurer of the Royal Asiatic Society of Bengal for the time being), the Managing Secretary (who shall be the General Secretary of the Royal Asiatic Society of Bengal for the time being), and five Ordinary Members elected by the General Committee. For the purpose of this election any Ordinary Member may propose the name of an Ordinary Member for election to the Executive Committee. Such proposal must be seconded by another Ordinary Member and must reach the General Secretary before the 15th September. The Executive Committee shall circulate these names, together with such other names not exceeding three, as it may suggest, to all Ordinary Members for election by ballot. The ballot papers will be scrutinized by the President and the General Secretaries, and the results of the ballot will be announced at the meeting of the General Committee.

The Executive Committee shall co-opt as Members at least one and not more than two Local Secretaries for the ensuing Session of the Congress.

14. The Executive Committee shall have full power to transact all business in cases of emergency, notwithstanding any limitations hereinafter laid down, and to deal with all matters not otherwise provided for in these Rules, including the making of such Regulations as may appear conducive to the good administration of the Association and the attainment of its object; provided always that such Regulations be not inconsistent with anything contained in these Rules, that they be reported for the information of the next meeting of the General Committee, and that they be subject to rescission or alteration by the Executive Committee or by any meeting of the General Committee.

15. There shall be a General Committee which shall consist of all Ordinary Members of the Association.

16. The General Committee shall meet at least once during each Session of the Congress preferably in the middle of the Session.

17. There shall be a Council which shall consist of all Members of the Executive Committee, and all such Ordinary Members of the Association as have held office as President, General Secretary, Treasurer, or Managing Secretary of the Association, the Sectional Presidents for the ensuing Session, and in addition five Ordinary Members of the Association elected by the General Committee. For the purpose of this election any Ordinary Member may propose the name of an Ordinary Member for election to the Council. Such proposal must be seconded by another Ordinary Member and must reach the General Secretary before the 15th September. The Executive Committee shall circulate these names, together with such other names, not exceeding three, as it may suggest, to all Ordinary Members for election by ballot. The ballot papers will be scrutinized by the President and the General Secretaries, and the results of the ballot will be announced at the meeting of the General Committee.

18. The function of the Council shall be to act as a body of advisers to be consulted by the Executive Committee on important questions of policy or scientific import.



19. There shall be a President who shall be nominated by the Executive Committee and whose nomination shall be submitted to the General Committee at its Annual Meeting during the Session of the Congress for confirmation.

20. There shall be two General Secretaries who shall be nominated by the Executive Committee and whose nomination shall be submitted to the General Committee at its Annual Meeting during the Session of the Congress for confirmation.

21. The term of office of each General Secretary shall be for a period of five years following the confirmation of his appointment and he shall be eligible for re-appointment.

22. In the event of a vacancy amongst the General Secretaries occurring between two Sessions of the Congress the Executive Committee shall have power to appoint a General Secretary for the period up to the termination of the next Session of the Congress.

23. There shall be a Local Secretary or Local Secretaries for each Session of the Congress who shall be appointed by the Executive Committee.

24. There shall be a Local Committee for each Session of the Congress which shall be appointed by the Executive Committee.

25. The Local Secretary, or Secretaries, and the Local Committee shall jointly, on behalf of and in consultation with the Executive Committee, make all necessary arrangements for the holding of the Session of the Congress.

26. For the purpose of scientific deliberation during the Session of the Congress there shall be such Sections corresponding to different branches of science as may from time to time be constituted by the General Committee on the recommendation of the Executive Committee.

27. There shall be Sectional Presidents and Sectional Recorders who shall be appointed by the Executive Committee.

28. There shall be Sectional Committees which shall consist of the following :—

- (a) The President of the Section (convener) ;
- (b) The Recorder of the Section ;
- (c) All Ordinary Members of the Association who have been President or Recorder of the Section concerned ;
- (d) Two Ordinary Members elected by the General Committee at its Annual Meeting during the Session of the Congress.

A Sectional Committee may co-opt two additional Ordinary Members of the Congress of whom one at least shall be resident in the locality in which the ensuing Session of the Congress is to be held.

29. The Sectional Committees shall meet on the opening day of each Session of the Congress and as often as may be necessary during the Session of the Congress.

In the absence of the President of any Section from any of its meeting the most senior member of the Sectional Committee present shall take the Chair.

Each Sectional Committee shall in its meetings during the Session of each Congress :—

- (a) nominate a Sectional President and a Sectional Recorder for next year's Session of the Congress for the consideration of the Executive Committee ;
- (b) determine the detailed arrangements of the Sectional meetings ;



- (c) select the papers to be read and discussed ;
- (d) delete by a two-thirds' majority any abstract from final publication in the Proceedings ;
- (e) determine the contents of the Sectional record in the Proceedings, observing the relevant provisions of Rule 30.

30. (a) Any paper submitted for reading at the Session of the Congress shall be forwarded to the President of the Section concerned so as to reach him not later than a date to be fixed from time to time by the Executive Committee.

(b) Any paper submitted for reading at the Session of the Congress shall be accompanied by an abstract in triplicate.

(c) Any paper submitted for reading at the Session of the Congress shall be refereed by the Sectional President or by some person or persons appointed by him. Decisions with regard to acceptance or rejection of any paper shall be final and all reports confidential.

(d) No paper published elsewhere shall be accepted.

(e) No abstract shall be published in the Proceedings if the complete paper has not been available for reading before the meetings of a Section.

31. The following procedure shall be observed for the making of any addition to or alteration in the Rules of the Association :—

(i) Proposals for additions to and alterations in the existing Rules may be placed at any time before the General Committee by the Executive Committee.

(ii) (a) Proposals for additions to and alterations in the existing Rules by any Ordinary Member of the Association shall be sent to one of the General Secretaries so as to reach him two full months before the meeting of the General Committee in which they are to be moved.

(b) One of the General Secretaries shall circulate such proposals to all Ordinary Members of the Association at least one full month before the meeting of the General Committee.

(c) Any amendments to the proposals shall be sent by any Ordinary Member of the Association to one of the General Secretaries so as to reach him at least a fortnight before the meeting of the General Committee.

(d) The proposals together with any amendments shall be brought up before the meeting of the General Committee at its Annual Meeting during the Session of the Congress together with any remarks of the Executive Committee and declared carried if accepted by a two-thirds' majority of the constituent Members present and voting at the meeting.

(Adopted the 5th January, 1931.  
Revised the 5th January 1935,  
and the 6th January, 1936.)



INDIAN SCIENCE CONGRESS (MODEL)

To

THE PRESIDENT.....

Section,

Twenty-fourth Annual Meeting of the Indian Science Congress,

Dear Sir,

As an Ordinary Member of the Indian Science Congress for 1936/37, I am forwarding herewith.....  
paper(s), which I intend to read at the meeting of your Section in the Indian Science Congress, accompanied by  
three typed copies of abstracts of each for submission to the Sectional Committee.

Yours faithfully,

IMPORTANT

Papers should be sent as early as possible. THEY ARE ONLY ADMISSIBLE TILL SEPTEMBER 15th.

Name.....

Address.....

Date.....







# INDIAN SCIENCE CONGRESS ASSOCIATION

## TWENTY-FOURTH YEAR

1st February, 1936—31st January, 1937

### LIST OF OFFICERS

#### EXECUTIVE COMMITTEE :

- |   |  |
|---|--|
| 1. Rai Sir Upendranath Brahmachari Bahadur, Kt., M.A., M.D.,<br>Ph.D., F.S.M.F., F.N.I., F.R.A.S.B. <i>President.</i> |  |
| 2. Rao Bahadur T. S. Venkataraman, B.A., I.A.S., <i>President Elect.</i>  |  |
| 3. W. D. West, Esq., M.A. (Cantab.), F.N.I.   | } <i>General Secretaries.</i>              |
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# INDIAN SCIENCE CONGRESS ASSOCIATION



FORTY-FIRST YEAR

1st February, 1953—31st January, 1954

**NOTICES**  
**LIST OF OFFICERS, SECTIONAL COMMITTEES**  
**AND ORDINARY MEMBERS**

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1, PARK STREET, CALCUTTA - 16

AUGUST 1953



### **NOTE**

The Final List of Members will be printed in Part IV of the Proceedings issued after the session of the Congress by the middle of the year.

Any inaccuracy or omission in the present list, if reported to the General Secretary, at 1, Park Street, Calcutta-16, will be rectified in the Final List.



# INDIAN SCIENCE CONGRESS ASSOCIATION

(Registered under Act XXI of 1860)

## FORTY-FIRST ANNUAL MEETING, 1954

### General Information

The Forty-first Annual Meeting will be held at Hyderabad-Deccan from January 2nd to January 8th, 1954.

Hon'ble Dr. B. Ramakrishna Rao, B.A., LL.B., D.Litt., Chief Minister, Government of Hyderabad and Chancellor, Osmania University, Hyderabad-Deccan, has kindly agreed to be the Patron of the Meeting.

Dr. S. L. Hora, D.Sc., F.R.S.E., C.M.Z.S., M.I.Biol., F.A.S., F.Z.S.I., F.N.I., will preside over the Meeting.

The names and address of the Sectional Presidents are given in the following pages.

### Local Arrangements

All enquiries about accommodation and other local arrangements should be addressed to the Local Secretaries, 41st Indian Science Congress, Osmania University, Hyderabad-Dn. Early intimation of the accommodation required should be sent to the Local Secretaries.

### Membership Cards and Literature

Ordinary Membership cards have been forwarded to all Ordinary Members.

A detailed provisional programme of the Forty-first Meeting of the Congress will be issued to all Ordinary Members in course of December of this year, together with a copy of Part III of the Proceedings containing Abstracts of the Paper accepted for reading at the different Sections.

Parts I (Official matters), II (Presidential Addresses) and IV (Discussions) of the proceedings will be issued by the middle of the following year.

## FORTY-SECOND ANNUAL MEETING, 1955

Subscription notice will be sent out to all Ordinary Members on the register after the 1st February, 1954. This will be followed, after a suitable interval, by the Ordinary Membership cards for the year,



1954-55 per V.P.P. for the amount of the subscription. Payment of the subscription fee of Rs. 12/- before the 15th July, 1954 will be only effective for continuance of Ordinary Membership during the ensuing year, covering the Forty-second Annual Meeting.

### **Application for Membership**

Application for new Ordinary Membership should furnish the following particulars. No form is necessary.

1. Name in full, with degrees and titles in block letters.
2. Appointment, designation or profession.
3. Full address where correspondence is to be made.

This should reach the office of the Association at 1, Park Street, Calcutta-16, on or before the 15th July, 1954.



# INDIAN SCIENCE CONGRESS ASSOCIATION

FORTY-FIRST YEAR: 1ST FEBRUARY, 1953—31ST JANUARY, 1954.

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(3) Prof. Alan Mara Bateman, 91-A Yale Station, New Haven, Conn., U.S.A.	Geology
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(5) Prof. Norbert Wiener, F.R.S., Department of Mathematics, Massachusetts Institute of Technology, Massachusetts, U.S.A.	Mathematics
*(6) Dr. Ing. R. Saliger, Professor of Reinforced Concrete Construction, University of Vienna, Austria.	Engineering
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(8) Prof. A. C. Hardy, F.R.S., Department of Zoology, Oxford University, U.K.	Zoology
*(10) Sir John Cockcroft, Director, Atomic Enginergy Establishment Research, Didcot, Harwell, Berks, U.K.	Physics
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# STUDIES IN THE DISEASES OF *MANGIFERA INDICA* LINN.

## Part V. On the Die-back Disease of the Mango Tree

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### INTRODUCTION

MANGO trees are subject to a disease in which the leaves fall off, twigs dry up, and the entire branch or the part affected assumes an appearance of dry, dead, leafless twigs sticking up from among the green healthy foliage resembling the 'die-back' and twig blight of trees commonly described in pathological literature. The disease is prevalent not only in the U.P. but also in other mango-growing provinces of India. A number of diseased twigs were collected from Lucknow and Madras, and the investigation was undertaken to ascertain the cause of the disease. The results are presented in this paper. A preliminary note was published earlier (Das Gupta and Zachariah, 1939).

### SYMPTOMS

*General.*—The effect of the disease on the general appearance of the trees is noticeable at anytime of the year ; but it is most conspicuous during the months of September and October. A large number of wilted branches and twigs are prominent among the green foliage of infected trees. In advanced stages of the disease leafless branches as well as twigs showing different stages of wilt give the tree an appearance as if it has been scorched by fire (Pl. V, Fig. 1). A magnified view of a portion of tree affected by the disease is shown in Pl. V, Fig. 2. Generally the smaller twigs and branches of comparatively old trees are affected.

*External.*—The first external evidence of the disease is the discolouring and darkening of the bark at a certain distance from the tip (Pl. V, Fig. 3a). The front and side views of the dark infected area are shown in Pl. V, Figs. 8 and 9. Such dark patches usually occur in the young green twigs and are hardly distinguishable in older branches.

As the darkening advances towards the tip the leaves just above the infected region wither (Pl. V, Fig. 3b). The upper leaves lose their healthy green colour and gradually turn brown (Pl. V, Fig. 4b). The browning starts at the base of the leaf, spreads along the midrib, and then out along the veins to the margin. This is followed by the browning of the whole leaf accompanied by the upward rolling of the margine (Pl. V, Fig. 5a). Eventually the affected twig or branch



dies and shrivels up (Pl. V, Fig. 4). A magnified view of the rolled shrivelled leaves is shown in Pl. V, Fig. 6. The brown rolled leaves often persist for a month or more (Pl. V, Fig. 7) and finally drop off, leaving the shrivelled twig altogether bare of leaves which is the characteristic of the advanced stage of the disease (Pl. V, Fig. 7*b*). Infection may be accompanied by the extrusion of gum (Pl. V, Fig. 9*j*).

#### HISTOPATHOLOGY

The infected twig shows an internal discolouration which is found to extend at an earlier stage of the disease about an inch on either side, towards the tip and the base of the twig, beyond the external darkened bark. The diseased twigs when cut out slantingly along the long axis through the infected region reveal a brown streaking of the vascular tissues, namely, cambium and phloem (Pl. V, Fig. 10). The internal discolouration is diffuse and uniform and appears as a dark streak between the stele and the cortex (Pl. V, Fig. 11). Series of sections of affected twigs showing different stages of the disease were examined to study the effect of the disease on the internal tissues.

Sections at about four inches below the growing point of a twig at a very early stage of infection which appeared healthy except for a short discoloured area on the stem showed slightly shrivelled, epidermal and sub-epidermal cells. The internal discolouration was manifested by the browning of certain regions of the cambium and phloem, where some of the cells were found to be plugged with a yellow gum-like substance. A few hyphæ were seen in the xylem vessels. The inner regions of the cortex appeared unaffected while the cells of the outer layers had started shrivelling.

In very advanced stages of the disease, the cells of the different tissues of the stem were badly shrivelled. The xylem vessels were plugged with fungal mycelium. The stele and the outer layers got separated from each other along the discoloured band at the cambial region where the cells had disintegrated. Numerous hyphæ were found in this region. A few hyphæ were also found in the cells of the cortex. The mycelium was found not only in the bundles of the stem, but also in the petioles and midribs of leaves of infected twigs.

#### EXPERIMENTAL

Infected twigs were collected from trees of the Botany Department, Lucknow University, and the Isabella Thoburn College Orchard, Lucknow. Material from Madras was collected by Dr. T. S. Sadasivan from trees showing variable symptoms of die-back.

Twigs showing different stages of the disease were chosen for the investigation. In some the leaves were just turning brown; in others they had completely shrivelled up. In very advanced stages the twigs were quite dry with no leaves on them. The surface of the bark showed leaf-scars, lenticels and breaks caused by natural cracking of the outer layers.

As isolation from infected twigs by taking small inocula from the internal diseased tissue and directly culturing them in nutrient



medium proved impracticable, the diseased twigs were first placed in moist chambers and the hyphæ growing out from the pieces were sub-cultured in the standard synthetic medium.

The infected twigs were first cleaned by swabbing with cotton-wool dipped in a saturated solution of borax. They were, then, cut into small pieces, 1-1½ inches long and each piece was separately washed in a saturated borax solution, steeped in 0.1% mercuric chloride for about five minutes, shaking vigorously at intervals and was finally washed in three changes of sterile distilled water. After this surface sterilisation, the twig pieces were placed in sterile moist chambers. A large number of twig pieces were tried with wood and bark intact, while other pieces had the bark stripped off from the wood portion and placed in separate moist chambers. Within 3-5 days these twig pieces showed a profuse growth of hyphæ in them. On an external examination only two types of hyphæ could be distinguished, one being pure white, the other whitish in colour at the beginning and turning dark with age.

Separate inoculations were made with hyphæ arising from different parts of the twigs pieces namely cut ends, surface of wood, inner and outer surfaces of bark, on standard synthetic medium and malt agar. By this method altogether five fungi were isolated, viz., *Botryodiplodia theobromæ* (B), *Phoma* (P), *Fusarium* (F), *Fusarium* (f), *Pestalozzia* (Pz), *Alternaria* (A).

The results are shown in Table I.

TABLE I

Locality	Twig 1			Twig 2			Twig 3			Twig 4			Twig 5			Twig 6		
	b&w	b	w	b&w	b	w	b&w	b	w	b&w	b	w	b&w	b	w	b&w	b	w
Botany Department	B	B	B	BF	BF	B	PF	PF	F	P	fA	P	P	Pz,f	P	PF	fA	F
Isabella Thoburn College	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Madras	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B

b & w=bark and wood, b=bark, w=wood.

On examination of the result it was found that all the six twigs belonging to different trees of the Isabella Thoburn College Orchard and those belonging to Madras showed the presence of *Botryodiplodia theobromæ* alone both from bark and wood whereas the twigs from the Botany Department garden gave anomalous results. The twig 1 produced only *Botryodiplodia theobromæ* from all its parts, the twig 2 produced *Botryodiplodia theobromæ* from wood only, but in bark, and bark and wood *Fusarium* was associated with *Botryodiplodia theobromæ*. Twigs 3, 4, 5 and 6 were characterised by the total absence of *Botryodiplodia theobromæ*, instead of which were found four different fungi,



*Phoma*, *Fusarium*, *Alternaria* and *Pestalozzia* either singly or variously associated. The last three were invariably associated with bark. In each case, however, the wood portion produced only one kind of fungus, for example, *Fusarium* in the wood of twigs 3 and 6 and *Phoma* in that of twigs 4 and 5.

It was apparent from this preliminary experiment that so far as the twigs from Isabella Thoburn College and those from Madras were concerned, the disease was due to *Botryodiplodia theobromæ*. But the appearance of more than one fungi from the wood of different diseased twigs of the mango tree of the Botany Department indicated that each of these fungi may be a potential parasite causing the disease.

Detailed work was next undertaken to confirm the results obtained : (a) by studying the spatial distribution of the fungal strains in diseased twigs, and (b) by inoculation experiments.

*Spatial distribution of fungi.*—The same experimental method as described before was employed. Twigs showing various stages of the disease and collected from localities already mentioned were surface sterilized. The diseased, and in some cases, apparently healthy parts were then divided into pieces 1–1½ inches in length (whenever possible bark was separated from wood) and put in moist chamber. The spatial distribution of the fungi in the twigs was found out by noting and drawing the exact position of the piece on the twig and numbering the successive pieces from the tip towards the base. A few leaves of each twig, too, were put in moist chamber after surface sterilisation. The fungi appearing from the twig pieces and leaves were inoculated on standard synthetic medium.

Although a very careful record was made of all the fungi which appeared from bark, and wood of different twigs tested, it was obvious that only the fungi growing out of the wood region, would be responsible for the disease. The fungi arising from bark or the surface of the wood would provide with subsidiary evidence regarding the causal organism. While analysing the results, therefore, greater attention has been paid to fungi isolated from wood portion.

*Botany Department Garden.*—Five twigs were employed, all belonging to the same tree. The description of the twigs indicating the extent to which disease has progressed is given below :

*Twig 1* (Text-fig. 1).—The upper part of the twig had been affected while the lower region remained green and apparently healthy. The affected part of the twig was slightly shrivelled and discoloured. There were no leaf-scars or wounds except a few superficial cracks of the bark. The leaves had wilted and turned brown. The twig was divided into five pieces.

*Twig 2* (Text-fig. 2).—This twig showed a more advanced stage of the disease. The stem as well as the leaves had completely dried up. The stem showed a few leaf-scars, lenticels and a scar left by a broken branch. It was divided into seven pieces.

*Twig 3* (Text-fig. 3).—This twig showed a very advanced stage of disease and the leaves had fallen off from one of the branches. There



were no leaf scars or wounds but lenticels were present. The upper end had a scar left by a fallen branch. It was divided into eight pieces. Four leaves were also tested.

*Twig 4* (Text-fig. 13).—The whole twig had been diseased and it showed a very advanced stage. The twig was completely dry and shrivelled. Leaf scars, branch scars and lenticels were found on the stem. All the leaves had fallen off except for a few on two small branches and these leaves, too, were brown and dry. The twig was divided into 24 pieces.

*Twig 5* (Text-fig. 5).—The entire twig had dried up and most of the leaves had broken off. Leaf scars and lenticels were present on the stem. The twig was divided into 10 pieces.

It will be seen from Text-figs. (1, 2, 3 and 13) that three out of the four twigs (Figs. 1–3) have produced *Botryodiplodia theobromæ* from wood from almost all the pieces. In twig 1 (Text-fig. 1) *Botryodiplodia theobromæ* has been found in the wood from the tip up to the base, excepting for one piece right at the end that gave only *Fusarium*. The two leaves tested from the top also gave rise to *Botryodiplodia theobromæ* only.

In twig 2 (Text-fig. 2) again *Botryodiplodia theobromæ* was present in the whole length of the diseased wood of both the branches tested, except two pieces at the end where mixed with *Botryodiplodia* there was *Phoma* in one and *Fusarium* in the other. The petiole of one leaf arising from the twig also gave *Botryodiplodia*.

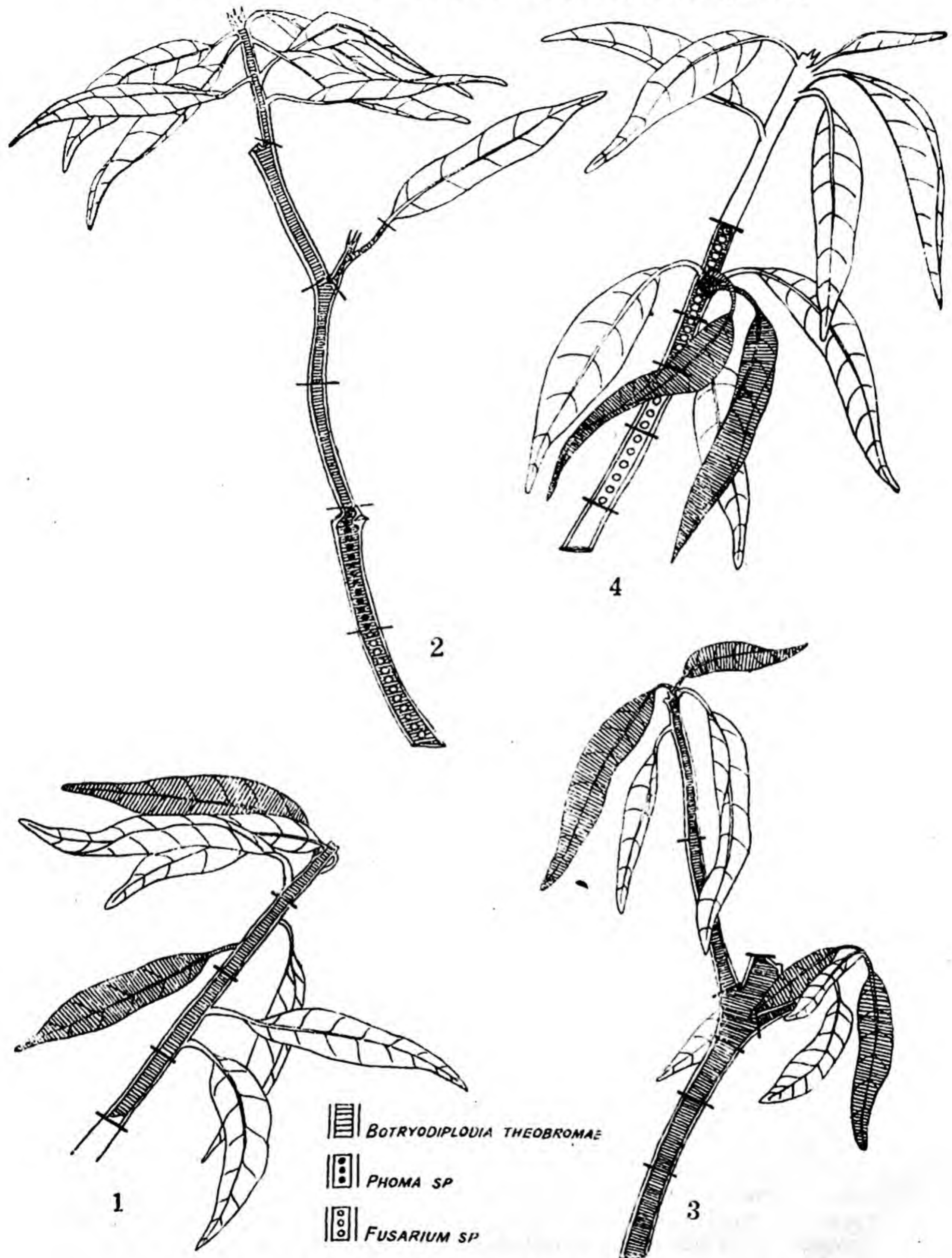
In twig 3 (Text-fig. 3) *Botryodiplodia* was found all along the wood in all the three branches except at the dry shrivelled end of one branch from which all the leaves had fallen off. This piece gave rise to *Fusarium*. All the four leaves tested also gave rise to *Botryodiplodia*.

Twig 4 (Text-fig. 13), however, which was completely shrivelled gave entirely different result. *Phoma* was found in the wood of all the branches right up to the petiole of the leaves, which were still persisting but along with this fungus was found associated in certain places, *Fusarium*. Comparison with bark fungi showed that *Fusarium* in all these cases must have come from bark.

Twig 5 (Text-fig. 5) also showed practically the same result as twig 4. *Phoma* was present almost throughout the diseased twig, excepting *Fusarium* and *Alternaria* in restricted regions.

It is apparent from the result that in the first three twigs it is the *Botryodiplodia theobromæ* that causes the disease, the other associated fungi are secondary. In twigs 4 and 5 *Phoma* seems to be the casual fungus and *Fusarium* only secondary. The two diseases in these two sets of twigs should therefore be considered as different. This disease due to *Phoma* has only been found in dry shrivelled twigs at the last stage of the disease and no early stage of infection by *Phoma* has been found. It is still to be seen if these may represent the blight disease of mango twig described by Kanitkar and Uppal (1939).





**Text-Figs. 1-4.** Figures illustrating spatial distribution of the fungi in the diseased mango twigs

**Figs. 1-3.** Twigs from Botany Department. **Fig. 4.** Twig from Isabella Thoburn College.



*Isabella Thoburn College Orchard*.—A large number of twigs were collected of which only six twigs from one tree, and two from two others representing various stages of the disease were selected for investigation.

*Tree 1, Twig 1* (Text-fig. 6).—The twig appeared healthy except for about two inches towards the lower end where it had turned black and slightly shrivelled. In this infected region there were leaf-scars and splits of the bark. The apparently healthy part of the twig was green and had a number of leaves and leaf-scars. The leaves though green were slightly pale and unhealthy looking.

The infected region was divided into two parts, the bark was removed from wood and each was put in a separate moist chamber.

*Tree 1, Twig 2* (Text-fig. 4).—The only evidence of infection in this twig was slight blackening of the bark at the lower node where two of the leaves had wilted. A small globule of gum was secreted in between the petioles of these two leaves. All the other leaves remained green and apparently healthy. The lower part of the twig was divided into four pieces.

*Tree 1, Twig 3* (Text-fig. 7).—This twig showed the initial stage of the disease. The infected region had turned black and two leaves at the upper end of the discoloured region had completely wilted. The part of the twig above the infected region had started wilting and the leaves were turning brown. The infected region was divided into 3 pieces and the apparently healthy part towards the apex into 4 pieces.

*Tree 1, Twig 4* (Text-fig. 9).—A slightly advanced stage of the disease was shown in this twig. The upper end of the twig was discoloured and a brown colour extended along the midrib of the leaves of the infected region. The two edges of the leaves folded inwards and in some cases there was also a twisting of the leaves towards the leaf-scars, lenticels and splits in the bark. Globules of gum were found at different spots. The diseased portion of the twig was divided into six pieces and three of the leaves were also tested.

*Tree 1, Twig 5* (Text-fig. 10).—The upper end of the twig was infected and the stem had turned brown. Leaf-scars, lenticels and a scar left by a fallen branch were present in the infected region of the twig. Gum was secreted a little below the branch scar. In the leaves, a brown colour extended along the midrib and margins which advanced inwards. The leaves rolled inwards and in some cases they had curled towards the tip. The infected region was divided into 8 pieces and three of the leaves were tested.

*Tree 1, Twig 6* (Text-fig. 11).—This twig showed a more advanced stage. Leaf-scars and lenticels were present in the infected part and a big globule of gum was secreted towards the lower end of the infected region. The leaves were all brown and shrivelled. The twig was divided into 9 pieces.

*Tree 2, Twig 1*.—A more advanced stage of the disease was shown by this twig. The stem as well as all the leaves had completely dried and shrivelled, and one branch was devoid of leaves. The twig was divided into 18 pieces.





Text-Figs. 5-8. Figures illustrating spatial distribution of the fungi in the diseased mango twigs

Fig. 5. Twig from Botany Department. Figs. 6 and 7. Twigs from Isabella Thoburn College. Fig. 8. Twig from Madras.



*Tree 3, Twig 1* (Text-fig. 12).—This twig showed a very advanced stage of the disease. The entire twig was completely dry and most of the leaves had broken off from the stem. It was divided into 15 pieces.

It will be seen from Text-figs. 4, 6, 7 and 9 to 12 that *Botryodiplodia theobromæ* is the most frequently occurring strain on eight different twigs belonging to three different trees. Twig. 1 (Text-fig. 6) shows the initial stage of infection and the infected region produces only *Botryodiplodia theobromæ*. The result from twig 2 (Text-fig. 4) is somewhat different although the twig is in early stage of infection. Two fungi are found associated together—*Botryodiplodia theobromæ* and *Fusarium*. *Botryodiplodia* is exclusively present in the leaves, and in the upper region of the infected part, but *Fusarium* extends to the lower portion of the diseased tissue where there is no *Botryodiplodia*.

In twig 3 (Text-fig. 7) *Botryodiplodia* is restricted to the lower region, i.e., the diseased part of the twig. *Fusarium* on the other hand is restricted to the wood of the upper region which externally appeared to be free from disease. The leaves, however, show a mixture of both the fungi.

In twig 4 (Text-fig. 9) where the disease had advanced further the leaves and the entire length of the wood gave *Botryodiplodia*, only a small portion showed the presence of *Fusarium*.

In twig 5 (Text-fig. 10) the wood of the upper portion along with the leaves gave *Botryodiplodia*, lower half only *Fusarium*.

In twig 6 (Text-fig. 11) showing still more advanced stage of the disease, almost the entire length is *Botryodiplodia* which is mixed with *Fusarium* only at the lower end. There is pure *Fusarium* further down.

In twig 1 of tree 2 *Botryodiplodia* is present all along the wood except at the tip and in the small portion at the middle where *Fusarium* and *Phoma* are found.

In twig 1, tree 3 (Text-fig. 12) the entire wood of the infected part showed only *Botryodiplodia theobromæ*.

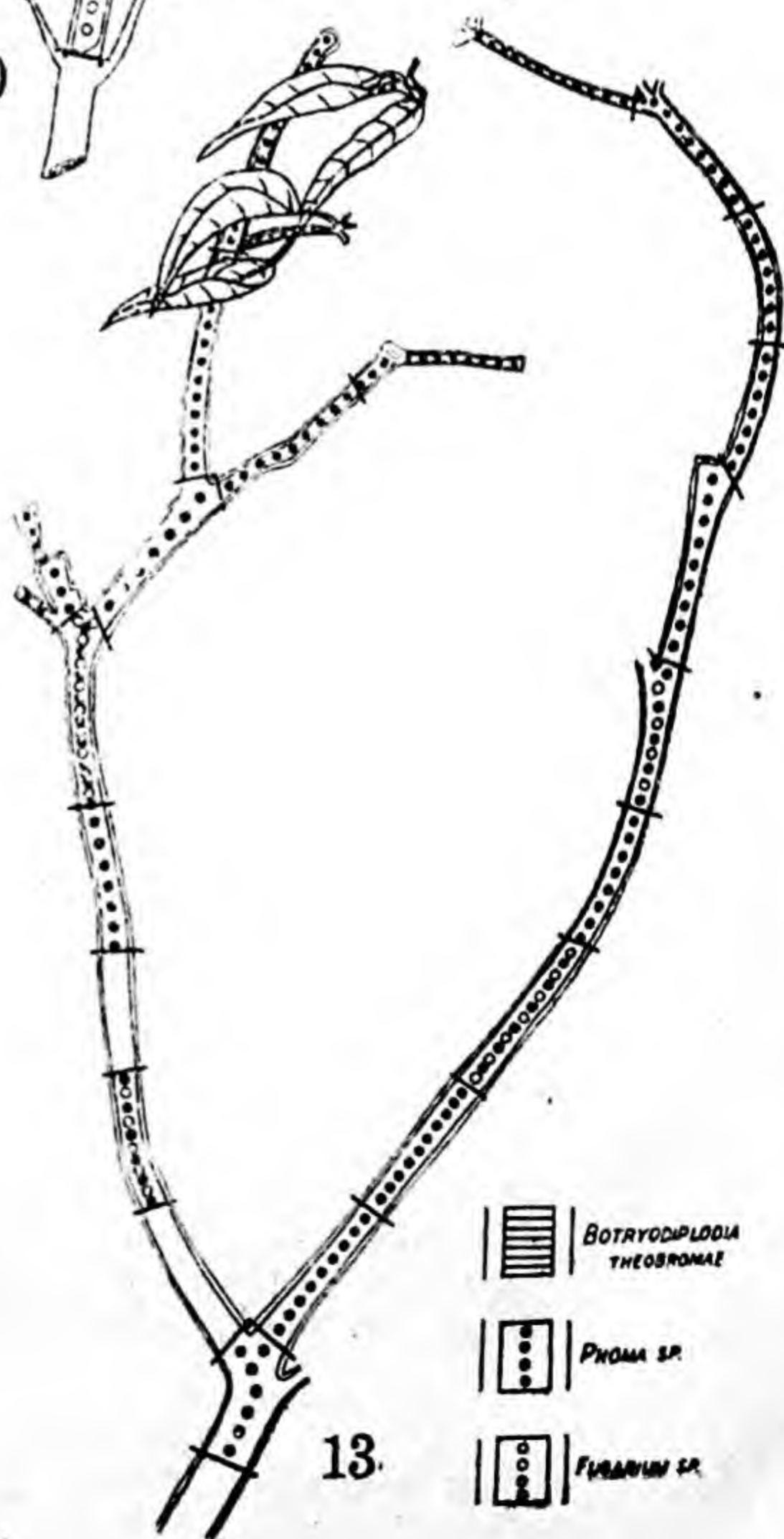
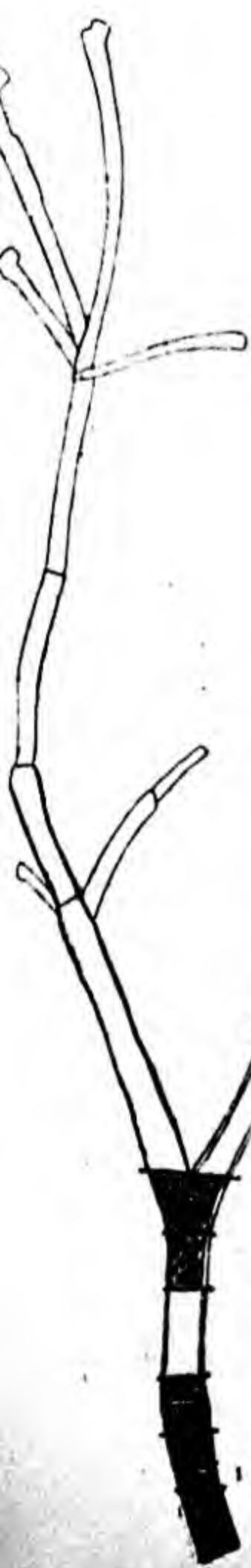
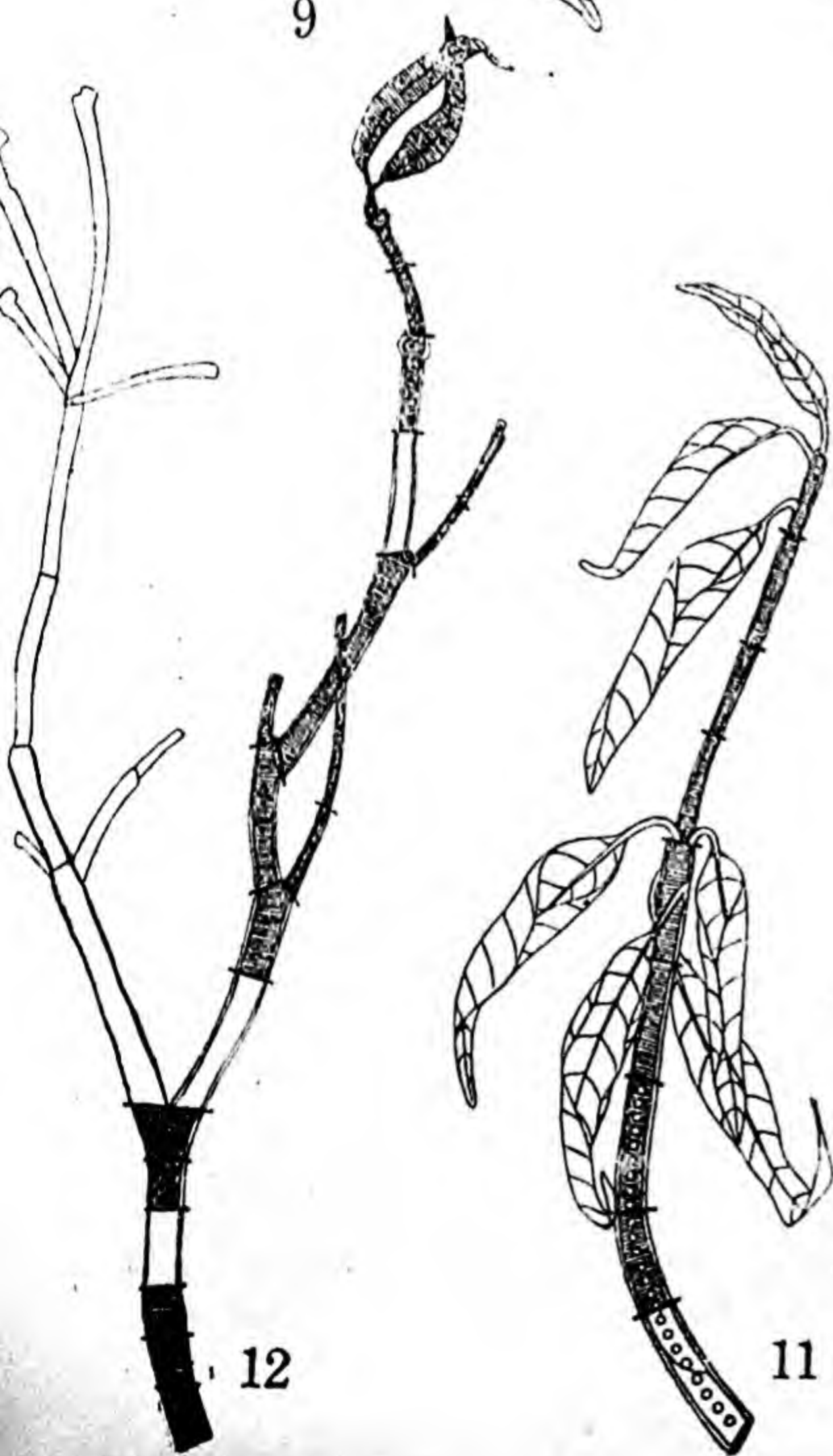
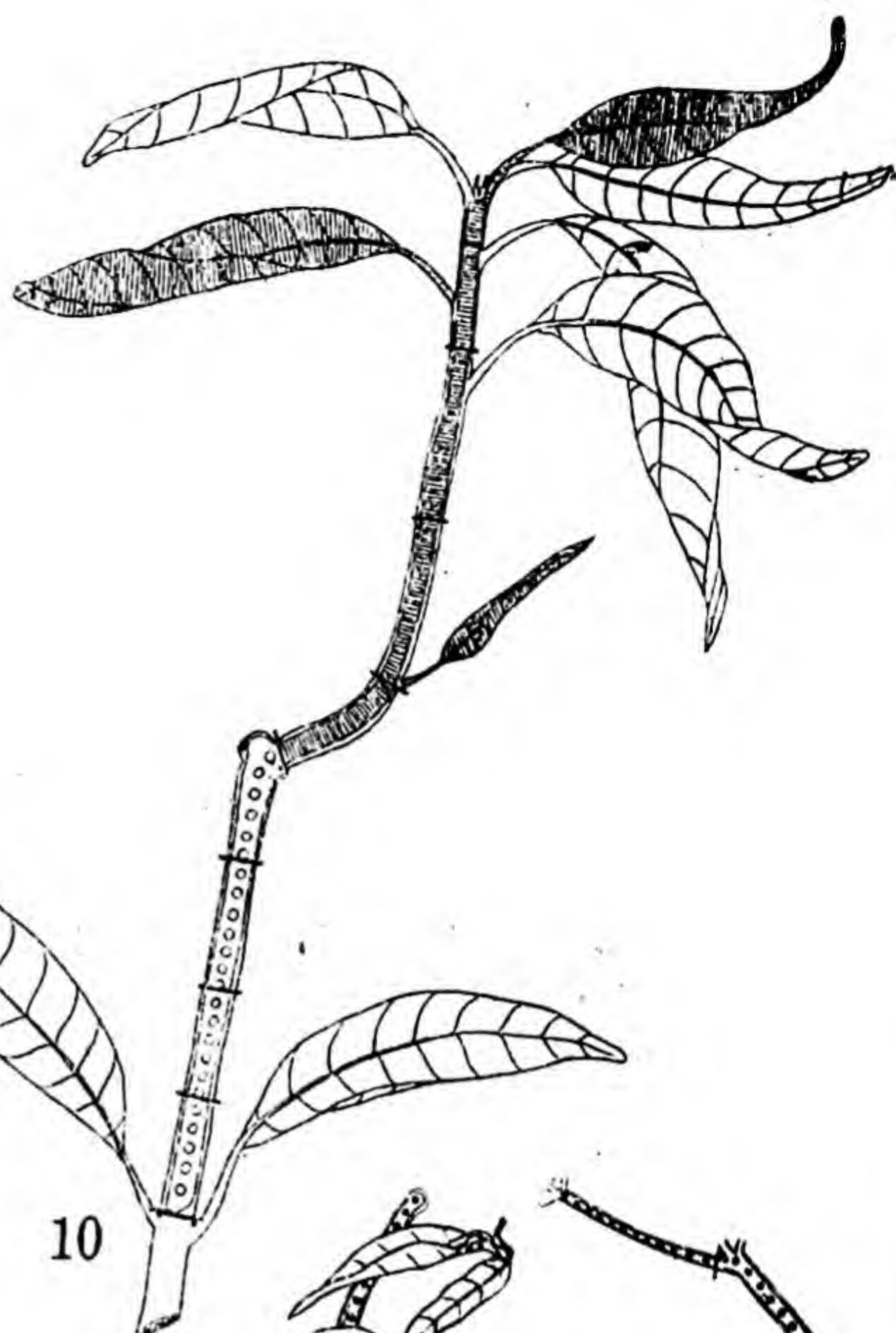
An analysis of the result shows that there is an overwhelming evidence that the disease in all these twigs is caused by *Botryodiplodia*.




*Madras twigs*.—Twigs obtained from Madras were all dry and showed an advanced stage of the disease. Five twigs were tested. All of these gave identical results. Text-fig. 8 shows one of these twigs. It was divided into 10 pieces and the bark was separated from wood in all cases except in the topmost piece. Two of the leaves in two different branches of the twig were also tested. *Botryodiplodia theobromæ* was the only fungus obtained from the diseased bark, wood and leaf (Text-fig. 8) and undoubtedly the cause of disease.

#### *Inoculation experiments*

*Mango plants*.—Forty mango plants were raised from seeds and grown in pots for inoculation tests to find out whether *Botryodiplodia*, *Fusarium* and *Phoma* could parasitise vigorously growing healthy seedlings. Monohyphal agar cultures of the different strains were used in all the inoculation experiments. The plants were inoculated after





- |   |  |
|---|--|
|  | <i>BOTRYODIPLODIA</i><br><i>THEOBROMAE</i> |
|  | <i>PHOMA</i> sp.                           |
|  | <i>FUSARIUM</i> sp.                        |



they had grown for five months. Most of the plants were about 1½ feet high while a few were only 1 foot in height.

The places to be wounded were first cleaned by swabbing with 0.1% mercuric chloride and then with sterile distilled water. An incision exposing the cells of the wood was made with a sterile scalpel and mycelium taken from the margins of agar cultures 3 days' old in *Botryodiplodia*, and 5 days' old in other 2 strains, was inserted in the wounds. Incised plants which received no inoculum served as controls. The wounded places were protected by wrapping with moist cotton and waxed paper. Of the 40 seedlings used, 10 replicates were made for each fungus—*Botryodiplodia*, *Phoma* and *Fusarium*, and the remaining 10 served as control.

None of the seedlings showed any sign of infection or wilting even though they were kept under observation for 6 months. A similar experiment with 40 seedlings next year also yielded negative results. Only *Botryodiplodia* was found to have produced in a few twigs slight canker near the inoculation point.

*Mango twigs.*—*Botryodiplodia*, *Phoma* and *Fusarium* were inoculated on healthy young twigs attached to the tree. Twenty-four twigs were selected for the purpose on the same tree. Six twigs were inoculated with each fungus and six served as control. Procedure adopted was the same as in inoculations on the young plants.

Out of six twigs inoculated with *Botryodiplodia*, three showed die-back symptoms on the 12th day after inoculation. All the twigs inoculated with the other strains remained unaffected. The three affected twigs on reisolation yielded only *Botryodiplodia*.

It will be seen from these inoculation experiments that all the four strains have failed to produce the disease on the inoculated young plants while *Botryodiplodia* is the only successful strain producing an infection of 50% on the inoculated twigs. Further inoculation experiments are in progress to find out the predisposing factors and the conditions under which the wounded parts get infected.

## DISCUSSION

The die-back of fruit and other trees is of common occurrence. Among stone fruit trees the disease is known to occur on almonds, apricots, peaches and plums (Cunningham, 1925), the causal organism, being *Clasterosporium carpophilum*. Die-back of apple branches due to *Glæosporium* sp. has been described by Wilkinson (1942).

The disease is also known to occur on Asiatic chestnuts which is caused by *Phomopsis* (Bedwell, 1937) and *Cryptodiaporthe castanea* (Tul.) Wehmeyer, *Botryosphæria ribis chromogena* G. and D. and *Diplodia* sp. (Fowler, 1938).

The white elm trees (*Ulmus americana* L.) in Nebraska is affected by die-back caused by *Cephalosporium* later identified as *Dothiorella ulmi* (May, 1931). The same disease in Elms in Minnesota is caused by a fungus which appears to be *Cytospora*.



As regards Gymnosperms, Curtis (1926) reported a die-back of *Pinus muricata* and *Pinus radiata* by the fungus *Botryodiplodia piniea* in New Zealand. The die-back of fir (*Pseudotsuga Douglasii* Carr.) has been attributed to the attack of *Sphaeropsis Ellisii* (Petri, 1913) and of *Pseudotsuga laxifolia* to that of *Diplodia pinea* (Waterman and Miller, 1936).

In India Petch (1916) has investigated the die-back of *Hevea brasiliensis* and die-back of tea plant of Ceylon which are ascribed to *Botryodiplodia theobromæ*. Sundararaman (1932) has reported die-back of cashewnuts by *Corticium salmonicolor*. This fungus according to him, is also known to attack mango, orange, jack-fruit, tea, coffee and several other trees. Narasimhan (1933-34) has reported *Diplodia* die-back of limes. Recently Kheswalla (1936) has reported die-back disease of fruit trees in Baluchistan by *Cytospora*. From a die-back of the tops of young Robusta coffee trees Mayne (1936) has isolated *Colletotrichum coffeanum*. Kanitkar and Uppal (1939) have given a short account of the twig blight of mango tree in Poona caused by species of *Phoma*.

In all these cases mentioned the disease is of fungal origin. But die-back may also be caused by bacteria, and by deficiency of salts.

The die-back of *Aucuba japonica* (Thunb.), for example, is caused by *Pseudomonas aucubicola* (Trapp, 1936). Ark and Thomas (1940) described the twig blight of apple tree in California in which he failed to find any pathogenic organism. On the other hand, the addition of boron and potassium in soil was found to reduce the die-back symptoms of the affected plants. Die-back of cloves in Zanzibar Protectorate is stated to be due to phosphorus and potassium deficiency owing to the deflection of these salts by grasses (*Ann. Rep. Dept. Agr. Zanz. Protectorate*, 1935, 1936).

Dwyer (1937) reports die-back deficiency disease in *Cocos nucifera* and also a physiological trouble affecting young palms which is characterised by a pronounced tip withering of the central leaves and drying-back of the outer leaves and pale-brown streaks on the back of the petioles.

Tubbs (1937) investigated factors affecting the die-back disease of tea, ascribed by Petch to *Botryodiplodia theobromæ* and is of opinion that the disease is of physiological origin and is associated with the deficiency in the production of carbohydrates; tea plants producing only half the carbohydrate necessary for their growth.

A number of fungi has been found to be associated with the die-back of mango trees here investigated. Leaving aside those which are exclusively found on the bark and are definitely saprophytic, there are three fungi *Botryodiplodia*, *Phoma* and *Fusarium*, which have claim to be regarded as causal organisms. Association of a large number of fungi in a tree affected with die-back is not unknown. Bedwell (1937) found *Sphaeropsis*, *Diplodia*, *Cytospora*, *Diplodina*, *Macrophoma*, *Fusicoccum*, *Dothiorella*, *Phoma* and *Epicoccum*, associated with twig blight of Asiatic chestnut, along with the more important pathogen *Phomopsis*.



The reconstruction of the exact position of the fungi in the twig pieces showed that *Botryodiplodia* was exclusively present in the wood of a number of twigs suggesting that the disease is due to *Botryodiplodia*. The pathogenicity of *Botryodiplodia* has also been demonstrated by inoculation experiment in which the fungus was able to infect mango twigs through wounds although no vigorously growing plant showed such infection.

It appears that the disease of other two twigs of the Botany Department is caused by *Phoma*. Although the result of the preliminary inoculation experiment is negative, the fact that the fungus has been found to be permeating the wood of the entire diseased twig almost exclusively seems to indicate the pathogenicity of *Phoma*. Further inoculation experiment is necessary to settle the point.

Kanitkar and Uppal (1939) have also found a species of *Phoma* causing twig-blight of mango trees. It is evident from the spore size that the two species are different.

The die-back or twig blight of the mango trees is caused definitely by *Botryodiplodia* and probably also by *Phoma*. It is not rare to find more than one organism causing die-back of the same species of tree. White elm in different parts of America is a case to the point.

The pathogenicity of *Fusarium* is, however, doubtful. There is no diseased twig from which the fungus alone has been isolated. When associated with other fungi, *Botryodiplodia* or *Phoma* it has almost always been found in restricted regions, the other fungus predominating. In such cases *Fusarium* must be considered as a secondary organism.

The same *Fusarium* found in the twigs of Isabella Thoburn College is pathogenically more significant particularly in two cases.

In tree 1, twig 2 *Fusarium* is not only associated with *Botryodiplodia* at the diseased portion of the twig but also occupies the wood of the diseased portion at the base, where no *Botryodiplodia* has been found. Of more significance is the twig 3 of the same tree. Here *Botryodiplodia* is restricted to the diseased portion only, whereas *Fusarium* exclusively occupies the apparently healthy portion of the twig from above the diseased portion right up to the tip.

The presence of *Fusarium* in advance of *Botryodiplodia* in the apparently healthy tissue up to the tip may point to its being a pathogen, or it may only indicate, that once having penetrated in the wake of the actual pathogen, *Fusarium* can advance more quickly inside the tissue.

There is thus a gradation in the pathogenicity of *Botryodiplodia*, *Phoma* and *Fusarium*, the three fungi intimately associated with die-back. The two fungi *Botryodiplodia theobromæ* and *Phoma* have often been found to be separately associated with *Fusarium*. The possibility that in such cases the disease is due to the combined activity of the two fungi, although *Botryodiplodia* and *Phoma* may produce the disease independently cannot be completely overlooked.

*Botryodiplodia* has been known to cause die-back in various plants, for example, *Pinus*, rubber, tea, etc., and also associated with leaf-break



of palm leaf, ring disease of palm nuts (Dwyer, 1937), diseased pods of cocoa (Baker, 1936) and storage diseases of grape fruits (Wardlaw and Leonard, 1937). It is not definite, however, if in all these cases the disease is due to *Botryodiplodia*.

The production of the die-back may be occasioned by unfavourable conditions acting as predisposing factors. In such cases the adverse conditions affect the growth and vitality of the tree in question which easily succumb to the invasion of otherwise harmless facultative parasites.

Münch (1935) is inclined to believe that the die-back of Larches is due to a fungus but not the fungus *Dasyscypha Willkomii* commonly associated in Germany with Larch Canker. Grimm (1937), however, is of opinion that the cause of dying off of Larches in Germany was due primarily to the disturbances of transpiration associated with adverse environmental factors; the trees thus weakened are readily accessible to infection by the Canker producing fungus. Day (1937) supports Langner's general conclusion (1936) that the fungus plays a secondary but a definite and necessary part in the development of the die-back and states that frost in this case is the predisposing factor.

Mayne (1935-1936) found that in the die-back of coffee tree the diseased shoots invariably showed the presence of *Colletotrichum coffeanum*, which was frequently the only fungus isolated. It was always found in shoots showing the very earliest external symptoms of the disease. But from field observations and the inconclusive inoculation experiments and other evidence he came to the conclusion that the primary predisposing factors in die-back are unfavourable conditions and premature leaf fall due to coffee-leaf-disease-fungus *Hemileia vastatrix*, and *Colletotrichum coffeanum* is only secondary to predisposing factors.

Müller (1936) describes that in the top die-back of coffee the presence of abundant shade of *Leucaena glauca* was observed to minimise the incidence of the disease. It is not improbable that high temperature in this case is the predisposing factor.

According to Dade (1937) swollen shoot of Cocoa is the result of extreme exposure of the tree to sun and wind during dry season, brought about by the gradual disappearance of shade trees and the surrounding forest (drought die-back). These weakened trees are invaded by secondary fungi such as *Botryodiplodia theobromæ* and saprophyte such as *Gliocladium roseum*, none of which can attack healthy tissue and produce necrotic die-back tissue with which these are always associated.

In the die-back of mango trees here investigated it seems that the fungi *Botryodiplodia* and *Phoma* are able to infect and produce the disease only in the less vigorous plants or twigs. It can well be that abnormal high summer temperature, 115° C., which sometimes kills twigs outright, is the predisposing factor.

The mode of infection and general symptoms of the disease are almost the same as described for other trees.



The infection in the "top die-back of coffee" caused by *Rhizoctonia* invariably commences in growing twigs and may frequently be detected before the hyphæ spread into stem. In the field the fungus travels from the leaves, through the wood vessels of the branches and stems. As a rule its diffusion is two to three times more rapid in an upward than in a downward direction (Müller, 1936).

In *Hevea brasiliensis*, the infection usually takes place not at the tip but at a variable distance from the growing point. The branch dies above the point of attack and less rapidly also backwards towards the base. As spread backwards occurs, the whorl of branches lower down are killed off in succession.

In the die-back of mango twigs caused by *Botryodiplodia* it has been found that the infection occurs at a node at variable distance below growing point, and the part of the twig above and below the point of infection dies. The leaves lose their healthy green colour and gradually turn brown. The browning starts at the base of the leaf and spreads along the midrib and then out along the veins to the margins. This is followed by the browning of the whole leaf, accompanied by the upward rolling of the margin.

In the white elm, the infection twigs show an internal streaking of the vascular tissues of the current season's growth. Goss and Frink (1934) have failed to find any external blackening of the bark above the point of infection although it has been described by May (1931) to occur on the Dutch Elm. In the infected mango twigs, the external blackening as well as internal streaking are clearly marked. The latter is seen as dark band between the xylem and cortex.

#### SUMMARY

The paper deals with the die-back disease of mango trees.

*Botryodiplodia theobromæ*, *Phoma* and *Fusarium* are the three fungi intimately associated with the die-back.

There is direct evidence from inoculation experiments that mango twigs can be infected and die-back produced by *Botryodiplodia*.

The evidence regarding the pathogenicity of *Phoma* is indirect, and based on the almost exclusive appearance of the fungus from some diseased twigs.

The pathogenicity of *Fusarium*, the other fungus associated with the disease, is not established.

These fungi are unable to attack vigorous healthy plants.

The predisposing factor in the case of die-back of Lucknow plants may be high summer temperature which affects the vitality of plants and enables the pathogens to attack.

The external symptoms and histopathology of die-back caused by *Botryodiplodia* have been given in detail.



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# EXPLANATION OF PLATE V

Figs. 1-2. Illustrating general aspect of a mango tree from Madras affected with die-back.

1. A diseased tree showing dead shrivelled twigs bare of leaves among green foliage.
2. A close-up view of the diseased tree in Fig. 1.

Figs. 3-5. Illustrating external symptoms of early stage of die-back.

3. (a) Discolouration and shrivelling of the infected region of stem. (b) Leaves above the point of infection withering.
4. (a) Shrivelled young twig; (b) upper three leaves have wilted.
5. (a) Infection at a node where all the leaves have wilted; (b) the leaves at the top apparently healthy.

Figs. 6-7. Illustrating external symptoms of advanced stage of die-back.

6. Characteristically curled leaves on the shrivelled twig enlarged.
7. Final stage of dead twigs. (a) Bunches of dry, curled leaves at the top; (b) twigs devoid of leaves.

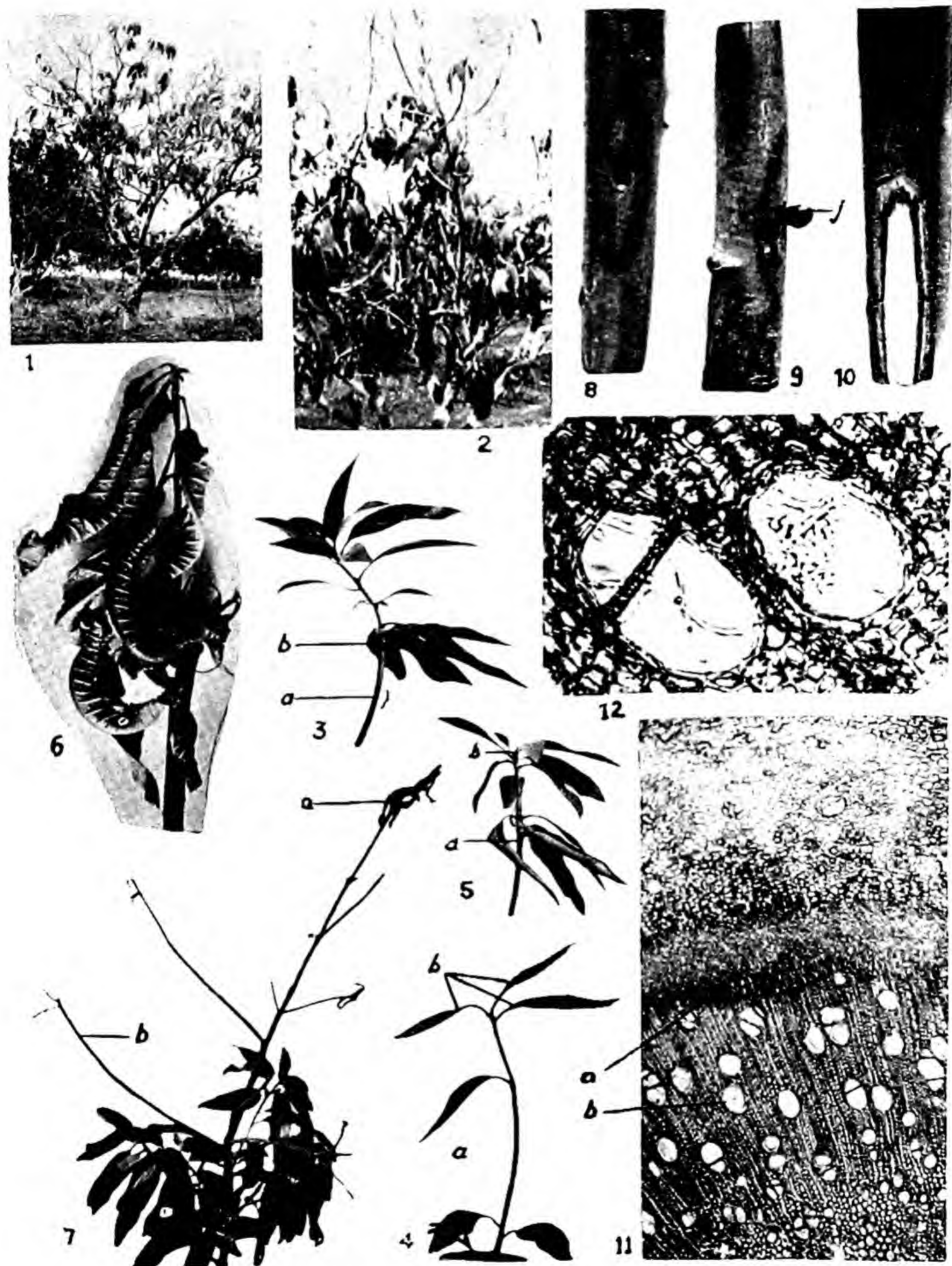
Figs. 8-10. Illustrating external symptoms at the early stage of infection.

8. Stem showing discolouration of the bark at the infected region—dark against green stem.  $\times 1.5$ .
9. Side view of Fig. 1 showing the discoloured infected region and the gum globule (g).  $\times 1.5$ .
10. Twig cut slantingly exposing the wood and internal streaking in phloem (p) and cambium (c).  $\times 1.5$ .

Figs. 11-12. Histopathology : advanced stage.

11. Section of old infected region.  $\times 52$ . (a) Brown deposits in phloem and cambium; (b) xylem vessels with fungal hyphæ.
12. Xylem vessels (of Fig. 11) enlarged to show the hyphæ inside.  $\times 330$ .





S. N. DAS GUPTA AND A. T. ZACHARIAH (MISS)—  
 STUDIES IN THE DISEASES OF *MANGIFERA INDICA* LINN.







## STUDIES IN THE DISEASES OF *MANGIFERA INDICA* LINN.

### VII. Latent Infection in the Mango Fruit

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#### INTRODUCTION

FRUITS of all stages beginning from the unfertilised ovary right upto the stage of maturity, as long as they are on trees, remain exposed to the atmosphere and come in direct contact with the fungal spores. Some of these spores lodge on the surface of the fruits, in the stomata or in the lenticels and continue in a viable condition without further development or in some cases germinate and produce infection hyphae. The infection hyphae penetrate the epidermis, pass into the tissues and remain dormant. These infections, although present in the fruits, are not detectable until such time as they produce the rot. It has, therefore, been termed as latent infection (Baker and Wardlaw, 1937).

It is, thus, expected that there must be a direct correlation between the fungi present in the orchard atmosphere, on the surface of the fruit and those present as latent infections.

In mangoes the problem of latent infections and its relation to the fungal flora of the orchards has been worked out by Baker and Wardlaw (1937) and Baker (1938). Sinha (Unpublished) working in this laboratory has shown that some of the storage rot in mangoes in Lucknow can be traced back to infection in the orchard and incidentally also the fungal flora in Lucknow mango orchards is considerably different from that in Trinidad. The work of Sinha as regards the orchard fungi has been extended by the present authors and the problem of latent infection has been worked out in detail for one fungus and the mechanism of latent infection and the mode of perennation of the fungus inside the fruit have been elucidated. The results are embodied in this paper.

#### MATERIAL AND METHOD

Two varieties of mango fruits—khajli and phajli—were mainly employed for the investigations. The distribution of the fungal organisms and its relation to the latent infection were studied for the Begumbagh orchard, in Lucknow.

The methods for the collection of the superficial fungi and the study of the fungal flora were the same as suggested by Baker and Wardlaw (1937). The standard synthetic medium was generally used, glucose agar being employed only for plating the surface washings of the mango fruits.



The artificial production of latent infection was attempted by two methods only, *i.e.*, the general spray of a concentrated conidial suspension and an application of conidia on superficial wounds. Samples of the experimental mangoes were periodically examined either in cuticular preparations by macerating the tissues in a mixture of potassium chlorate and nitric acid or in microtome sections, 16  $\mu$  thick, unstained or stained with Fleming's triple stain.

### ORCHARD FUNGI

The distribution and concentration of fungi in the orchard were found out by exposing plates with the standard synthetic medium, in triplicates for a period of two minutes, at a height of 6 feet, at the four selected spots in the Begumbagh orchard at definite intervals covering the entire mango season. The exposed plates were brought to the laboratory in sterile containers and incubated at the room temperature. When after 3 or 4 days colonies had appeared they were carefully counted and each one was separately subcultured. Most of the cultures sporulated and could be identified, only a few remained infertile.

All together 13 different fungi—*Aspergillus nidulans*, *Aspergillus niger*, *Aspergillus* sp., *Acrothecium penniseti*, *Acrothecium* sp., *Alternaria* sp. 1 and sp. 2, *Spondylochladium* sp., *Fusarium* sp. 1, sp. 2, and sp. 3, *Penicillium* sp. and *Rhizopus arrhizus* are found to occur in the atmosphere of the orchard.

Some of these, *e.g.*, *Aspergillus nidulans*, *Aspergillus niger* and *Fusarium* sp. 1 and 2 occurred regularly throughout the season, though their relative concentrations varied with time. Other fungi only made an occasional appearance—*Penicillium* sp. only on two occasions, *Aspergillus* sp. and *Spondylochladium* sp. three times and *Rhizopus arrhizus* four times.

There is a good deal of variation in the number of colonies appearing at different times of the mango season and it is difficult to correlate the results as the factors affecting the concentration of the fungal spores in the orchard are many and variable.

Concentration of *A. nidulans* is greatest in the first three exposures, *i.e.*, from April to the third week of June, the period during which the fruits are small or are gradually passing into the medium stage. *A. niger* and *Fusarium* sp. 1 begin with a high concentration which gradually falls and again rises. *Alternaria* sp. 1 and *Acrothecium penniseti* are fairly common and *Alternaria* sp. 2 and *Acrothecium* sp. 2 follow next.

### SURFACE FUNGI

The fungi present on the outer surface of the mango fruits of different stages of maturity were obtained by washing the surface of the fruits under aseptic conditions using the method described by Sinha (Unpublished). The results are presented in Table I.



TABLE I

*The concentration of fungi on the surface of mango fruits  
(total of 50 mangoes)*

Strains isolated	Frequency of occurrence of the colonies					Total of 50 mangoes
	28-4-42	7-5-42	13-6-42	20-6-42	27-6-42	
<i>Aspergillus nidulans</i> ..	57	37	119	41	29	283
<i>Aspergillus niger</i> ..	..	8	18	64	21	111
<i>Aspergillus</i> sp. ..	..	..	13	7	6	26
<i>Acrothecium</i> sp. ..	..	..	..	51	60	111
<i>Alternaria</i> sp. ..	9	..	59	32	28	128
<i>Fusarium</i> sp. 1 ..	12	6	12	..	6	36
<i>Fusarium</i> sp. 2 ..	..	15	6	..	4	25
<i>Rhizopus arrhizus</i> ..	..	..	3	..	3	6
<i>Penicillium</i> sp. ..	..	..	1	..	1	2

The surface washing yielded 9 fungi. Among these strains *A. nidulans* was present constantly, the concentration being fairly large during the early periods which shows a slight decline when the fruits approach maturity. *A. niger* is absent during the earliest sample. *Alternaria* sp. and *Fusarium* sp. 1 are fairly common whereas *Acrothecium* sp. appeared towards the later part of the season. *Rhizopus arrhizus* and *Penicillium* sp. are much less frequently found. Sinha (Unpublished) could obtain only five fungi as the surface isolates. In the present investigations *Neocosmospora vasinfecta* was absent.

The concentration of the surface fungi shows no definite relation to time. But it will be noted that when the net charge of the fungal spores on the total number of 50 fruits is taken into consideration, the four fungi—*Aspergillus nidulans*, *Aspergillus niger* and *Acrothecium* sp., *Alternaria* sp. stand out prominently. *Fusarium* sp. 1 although shows a low concentration, is a pathogen which is present in quite a high concentration in the early season.

#### ISOLATION OF LATENT FUNGI

Latent fungi were isolated from surface sterilized mangoes of all stages beginning from the unfertilised ovary to the fully mature fruit just before the time of picking. The materials were surface-sterilised by washing them in a concentrated solution of borax for 20 minutes, steeping them in 0.1% mercuric chloride for three to five minutes according to the stage of maturity and finally washing them several times in sterile distilled water. Surface washings of the fruits treated in this manner were found to be free from viable fungal spores. In the case of smaller fruits, the whole of the fruit was cut into pieces, and all the pieces were put on the standard synthetic medium. In the larger fruits, five cubes were rapidly taken out by means of a sterilised scalpel—2 from the upper tip, 2 from the equatorial region and one from the base. The fungi appearing after four days were recorded



and isolated in tubes. Pure cultures of the strains were obtained by subculture of monohyphal tips. The results are presented in Table II.

TABLE II

*The fungi isolated from apparently healthy fruits of varieties Khajli and Phajli*

Stage of maturity of fruits (length in mm.)	No. of fruits used for isolation	Number of fruits giving the strains				
		<i>Aspergillus nidulans</i>	<i>Aspergillus niger</i>	<i>Acrothecium</i> sp.	<i>Alternaria</i> sp. 1	<i>Fusarium</i> sp. 1
<i>Var. Khajli</i>						
Fertilised and unfertilised ovaries ..	30	..	..	..	..	22
3-5 ..	16	..	..	..	1	11
10-20 ..	20	1	..	..	1	..
30-55 ..	23	5	3	3	1	..
60-75 ..	15	5	1	..	..	..
75-95 ..	23	7	1	1	1	..
100-120 ..	17	6	2	..	..	1
Above 120 ..	14	4	2	..	1	3
Total ..	158	28	9	4	5	37
<i>Var. Phajli</i>						
Fertilised and unfertilised ovaries ..	20	..	..	..	..	15
3-10 ..	10	..	..	..	..	7
15-30 ..	20	..	2	..	1	7
30-50 ..	16	3	1	1	..	1
60-75 ..	15	4	2	1	..	..
75-95 ..	18	5	2	2	1	..
100-120 ..	13	4	2	1	1	..
Total ..	112	16	9	5	3	30

From the data presented in Table III it will be seen that out of 158 Khajli fruits, five fungi, viz., *Aspergillus nidulans*, *Aspergillus niger*, *Fusarium* sp. 1, *Acrothecium* sp. 2, and *Alternaria* sp. 1 were obtained, the first three being more important. In the number tested 28 fruits gave *Aspergillus nidulans*, 9 *A. niger*, 4 *Acrothecium* sp. 2, and 5 *Alternaria* sp. 1 and as many as 37 *Fusarium* sp. 1. It will also be noted that most of the *Fusarium* sp. was obtained from the young unfertilised ovaries or from fruits 3-5 mm. in length. Its absence in the later stages is probably due to its being pathogenic with the result that the unfertilised ovaries and the young fruits infected with the fungus do not develop further. The first appearance of *A. nidulans* is made when the fruits are 10-20 mm. in length but only from one



fruit. Five fruits out of a number of 23 from the next stage (30–35 mm.) yielded *A. nidulans*.

The same fungi were isolated from the 112 Phajli fruits, viz., *A. nidulans* from 16, *A. niger* from 9, *Acrothecium* sp. 2 from 5, *Alternaria* sp. 1 from 3 and *Fusarium* sp. 1 from 30 mangoes. As before *Fusarium* mainly appeared in the earliest stage.

A comparison of the orchard fungi with Tables 1 and 2 shows that the 5 latent fungi are common with 9 occurring on the general surface and the 13 recovered from the orchard atmosphere.

#### ARTIFICIAL PRODUCTION OF LATENT INFECTION

Experiments were carried out to cause latent infection artificially and also to determine the period at which it takes place in nature. Only one strain, *A. nidulans*—the most commonly occurring fungus—was selected. This fungus in the later part of the season showed saltations in some culture plates but the infection and other investigations were continued with the original non-saltating strain. Two methods were employed.

(a) *Spray inoculation*.—The fruits of the two varieties while on trees were surface sterilised with rectified spirit and a spray of a concentrated conidial suspension of *A. nidulans* in 0.5% malt extract given for three successive days (for a few minutes every day) and left on trees without any attempt being made to guard the fruits against natural infection.

Most of the fruits remained healthy; some, however, showed dry-rot in which the fruit shrivels up considerably, the skin together with the inner tissue is thrown into numerous folds, and becomes very hard. Subsequent investigations have indicated that the disease is not due to *A. nidulans* but a physiological one. The problem is under investigation.

The apparently healthy fruits (the fruits that did not show any external sign of the disease even 14 days after the spray) were investigated for possible latent infection. A fixed number of fruits were brought to the laboratory and after thorough surface sterilization representative areas were placed in plates with the standard synthetic medium to recover the fungus present in the fruits.

As it was not possible to take the weight of the fruits at the time of artificial infection, an arbitrary division of the different stages of maturity was based on the length, i.e., fruits below 75 mm. were termed as small (S), between 75 and 100 as medium (M) and above 100 as big (B). The results of the spray infection experiment on the two varieties are shown in Tables III and IV.

Tables III and IV show that small Khajli mangoes when sprayed with a concentrated conidial suspension, give 71.4% of latent infection. In the medium size, there is a considerable fall to 20.0% and in the big to 7.6%. The Phajli fruits gave more or less similar results, the percentage of infection being the greatest when the fruits are small, the later stages being less affected.



TABLE III

*The effect of spray of concentrated conidial suspension of A. nidulans on Khajli fruits of different stages of maturity*

Stages of maturity (Length in mm.)	No. of fruits sprayed	No. of diseased fruits after 14 days	No. of apparently healthy fruits	No. of fruits left on trees for future observation	No. of apparently healthy fruits planted	No. of fruits giving <i>A. nidulans</i>	Final percent- age of latent infection
<i>Experimental</i>							
S (below 75) ..	42	18	24	17	7	5	71.4
M (between 75-100) ..	48	1	47	28	19	4	21.0
B (above 100) ..	56	..	56	30	26	2	7.6
<i>Control</i>							
S (below 75) ..	20	3	17	9	8	1	12.5
M (between 75-100) ..	23	..	23	11	12	1	8.3
B (above 100) ..	31	..	31	14	17	1	5.8

TABLE IV

*The effect of spray of concentrated conidial suspension of A. nidulans on the Phajli fruits of the different stages of maturity*

Stage of maturity (Length in mm.)	No. of fruits sprayed	No. of diseased fruits after 14 days	No. of apparently healthy fruits	No. of fruits left on trees for future observation	No. of apparently healthy fruits planted	No. of fruits giving <i>A. nidulans</i>	Final percent- age of latent infection
<i>Experimental</i>							
S (below 75) ..	51	18	33	24	9	6	66.6
M (between 75-100) ..	32	2	30	15	15	3	20.0
B (above 100) ..	27	..	27	15	12	1	8.3
<i>Control</i>							
S (Below 75) ..	25	5	20	13	7	1	14.1
M (between 75-100) ..	20	1	19	10	9	2	22.2
S (above 100) ..	18	..	18	6	12	1	8.3

Latent infection was also found in similar unsprayed sets, being 22.2% in the medium Phajli fruits and 12.5% in the small-sized Khajli.

The results show that at an early stage of development when the fruits are small the fungus can lodge itself securely in the fruit as latent infection. But apparently in the medium and big fruits the fungal spores are unable to get a hold. Spraying at the later (medium and



big) stages, therefore, does not make any appreciable difference regarding latent infection.

The 109 Khajli and 83 Phajli fruits, left on trees for further observations on latent infection after the spraying treatment, showed that all of them remained healthy till they were on trees. Towards the end of the season, these mangoes were removed to the laboratory where they were surface sterilised by borax and mercuric chloride and wrapped in sterile papers, the stalk-end being sealed with wax to minimise loss due to evaporation in storage. The fruits were incubated in glass cases at the room temperature. The mangoes were examined after 9 days for rotting. The results are given in Table V.

TABLE V

*The number of uninfected and artificially infected fruits rotting in storage (Khajli and Phajli)*

Stage of maturity at which infected (Length in mm.)	Experimental		Control	
	No. of fruits stored for ripening	No. of fruits showing rotting after 9 days	No. of fruits stored for ripening	No. of fruits showing rotting after 9 days
<i>Var. Khajli</i>				
(S) Below 75 ..	11	8	6	1
(M) Between 75-100 ..	14	3	7	2
(B) Above 100 ..	21	4	9	2
Total ..	46	15	22	5
<i>Var. Phajli</i>				
(A) Below 75 ..	9	7	6	1
(M) Between 75-100 ..	10	2	6	1
(B) Above 100 ..	7	1	4	..
Total ..	26	10	16	2

An examination of fruits, 5 days after storage, showed 6 to 8 greyish-black lesions distributed on the general surface of the fruits. Nine days later most of them had coalesced to form one big or 2 to 3 smaller rotting patches.

It will be seen from Table V, that out of 46 Khajli fruits, inoculated by the spray method at different stages of maturity, 15 of them rotted 9 days after storage and that mangoes below 75 mm. proved more susceptible. A comparison of Table V with Tables III and IV shows that the percentage of artificial infection obtained by plating the sprayed fruits is near about 70% in stage 'S' and 20% in stage 'M'. Nearly the same rotting percentage is given by the artificially infected fruits stored for ripening. The results, thus, indicated clearly that the



fungus, *A. nidulans* remained latent as long as the fruits were on trees and caused rotting during storage by becoming active pathogen.

TABLE VI  
*The effect of wound inoculation of Khajli fruits  
by Aspergillus nidulans*

Stage of maturity (Length in mm.)	Total No. of fruits inoculated	No. of dis- eased fruits after		No. of apparently healthy fruits left on trees	No. of fruits plated after 14 days	No. of fruits giving <i>A. nidulans</i>	No. of fruits stored for ripening	No. of fruits rotted	Final percentage of latent infection
		14 days	2 months before trans- fer to storage						
<i>Experimental</i>									
S (below 75) ..	21	1	..	20	7	7	6	6	100.0
M (between 75-100) ..	39	1	3	38	15	13	9	9	91.6
B (above 100) ..	42	..	2	42	17	17	7	6	95.8
<i>Control</i>									
S (below 75) ..	10	..	..	10	4	..	4	..	..
M (between 75-100) ..	23	..	..	23	13	2	9	3	22.7
B (above 100) ..	24	..	..	24	13	2	8	1	14.2

TABLE VII  
*The effect of wound inoculation of Phajli fruits  
by Aspergillus nidulans*

Stage of maturity (Length in mm.)	Total No. of fruits inoculated	No. of diseased fruits after		No. of apparently healthy fruits left on trees	No. of fruits plant- ed after 14 days	No. of fruits giving <i>A. nidulans</i>	No. of fruits stored for ripening	No. of fruits rotted	Final percentage of latent infection
		14 days	2 months before trans- fer to storage						
<i>Experimental</i>									
S (below 75) ..	15	3	..	12	4	4	8	8	100.0
M (between 75-100) ..	29	4	..	25	12	12	9	8	95.2
B (above 100) ..	20	..	1	20	12	10	8	7	85.0
<i>Control</i>									
S (below 75) ..	12	2	..	10	4	..	4	..	..
M (between 75-100) ..	17	1	..	16	9	2	3	1	25.0
B (above 100) ..	15	..	..	15	9	..	2	..	..



(b) *Wound inoculation*.—The method consisted in making superficial punctures, involving minimum depth, in small areas on the mango fruits of different age while on trees and putting the inoculum of *A. nidulans* on the wound. This method ensures the entry of the fungus in the fruit. Fourteen days after infection representative parts from the inoculated areas of some of the fruits were examined in culture and the rest were brought to storage after two months. All the mangoes showed *A. nidulans* from the infected parts excepting two Khajli of the medium size and two Phajli of the big size. The results are given in Tables VI and VII.

#### STATE OF THE FUNGUS DURING THE PERIOD OF LATENCY

*By spores*.—To study the mode of perennation, the sprayed fruits were periodically examined in cuticular preparations and both in hand and microtome sections. It was found that in most cases the conidia were abundantly present and remained quite firmly lodged, on the general surface of the fruits as was also found by Kidd and Beaumont (1925) for apples. In two preparations only, conidia of *A. nidulans* and the hyphæ produced from them were also found in the substomatal cavity (Text-figs. 5 and 6). In the substomatal cavities, however, the conidia and the hyphæ remain well protected from the weather fluctuations until conditions become favourable for their germination and lateral spread. It may be mentioned that older fruits showed conidia only round about and on the lenticels but none in their cavities. Sinha (1945) has pointed out that in the mature condition the lenticels become covered over by the extension of the cuticle of the fruit.

*By hyphæ*.—The hyphæ of limited growth, presumed to be of *A. nidulans*, that remain dormant in the subcuticular region, are of more common occurrence (Text-figs. 4 and 5 b). Similar hyphæ whose identity has been definitely established by culture as *A. nidulans* have also been detected in the ducts and the cells of the outer-mesocarp (Text-figs. 7 and 8) of the fruits which were artificially infected at the stage 'S' (about 70 mm. in length) and gathered for investigations about the time of picking. It is, therefore, very likely that the hyphæ detected at the two places and at two different stages of maturity of the fruits are the same and that the subcuticular hyphæ resume their growth a little before the fruits are removed for storage.

That the fungus remains confined to the superficial layers is also proved by the fact that fresh surface sterilised cubes from mangoes, previously sprayed with the conidia of *A. nidulans*, when cut into hand sections and plated serially, invariably gave the fungus from the first two sections.

*Penetration of the infecting hypha*.—As most of the conidia are found to be present on the surface of the fruits (only a few in the substomatal cavity) and the hyphæ in the sub-cuticular region are considered to be the form in which the fungus survives the period of latency, it was thought desirable to study the mode of entry of the fungus into the mango tissue. There were two obvious methods for penetration: (i) the entry of the conidia lying near the stomata and the



lenticels into the cavities by means of germ tubes and (ii) the penetration of the cuticle by the infection hypha. For this purpose surface sterilised small fruits were placed in sterile moist chambers and inoculated with the conidia of *A. nidulans* at a number of places on the areas marked. The tissues from the marked areas were removed at regular intervals and fixed instantaneously for microtome sections and cuticular preparations by macerating the tissues in a mixture of potassium chlorate and nitric acid. It was noticed that the germ-tube from the conidia, on germination, spreads laterally on the skin (Text-fig. 1) until it makes its entry by a puncture in the cuticle (Text-fig. 2). The infecting hypha traverses the thickness of the cuticle where it meets the epidermis when it takes a turn (Text-fig. 3) and lodges itself between the cuticle and the epidermis (Text-fig. 4). Further growth of this hypha is arrested at this stage and it appears that due to certain factors, operating within the tissues, the hypha is unable to overcome the resistance offered by the innermost layers of the cuticle. A closer examination revealed that the cuticular layer is stratified as if one layer is deposited over the other. The one in immediate contact with the epidermal cells is denser and at times yellower which gradually thins out towards the periphery. Probably this difference determines the position taken by the hyphae which may either lie against the outer epidermis or slightly above it. The subcuticular hypha remains in a dormant condition without proceeding further until the lowering of the tissue resistance due to various physical and chemical changes associated with growth and senescence of the fruits.

There is no structure comparable to the appressorium found in the present fungus as is reported for *Colletotrichum* by Dey (1919) and Simmonds (1941). Many hyphae may infect the same fruit at a number of places. No external lesions or anthracnose spots could be noticed in the sprayed fruits but in the laboratory experiment small orange coloured areas developed where the hyphae entered the cuticle.

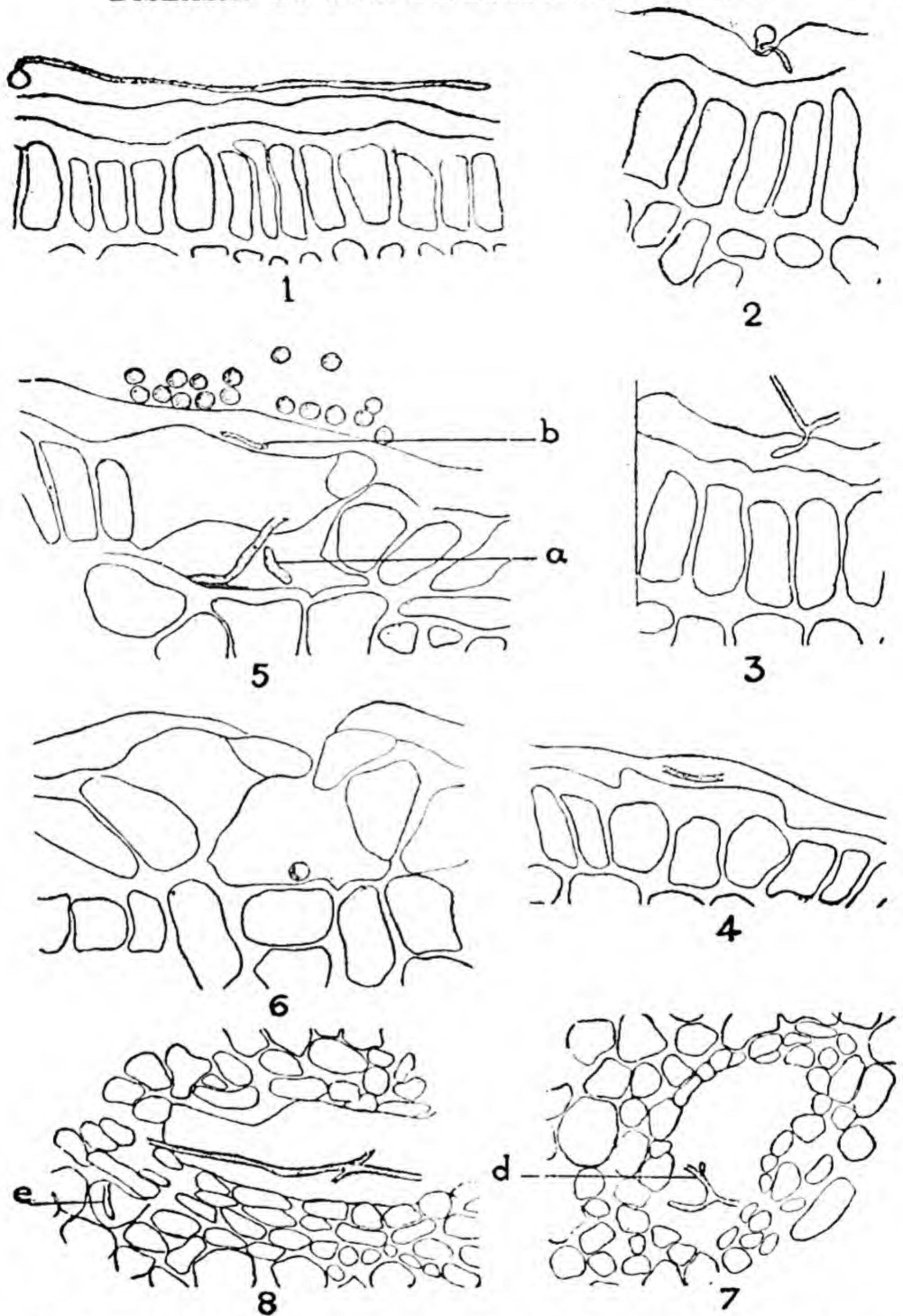
#### REACTION OF THE TISSUES TO THE PATHOGEN

The evidence available on the latent infection indicates that the development of the fungus is arrested at a very early stage and the infections are confined to the surface layers of the skin. Experiments were conducted to elucidate the reactions of the different tissues of the mangoes (epicarp and mesocarp).

With this end in view, an equal amount of inoculum, taken from the growing edge of the culture of *A. nidulans*, was introduced into fruits at three depths in the laboratory: (i) just below the green skin, (ii) at a depth of 5 mm. and (iii) on the stone.

For the last two sets, a method suggested by Granger and Horne (1924) was used, whereas for the first, a small peeling of the green skin was taken out by means of a sterile scalpel on three sides. After inoculation of the fungus, the peeling was replaced and sealed with wax. 22 Fruits were employed for each set. The fruits were examined after 2 weeks, the diseased part scraped out and weighed, eliminating





Text-figs. 1-8. Demonstrating the course of the infecting hypha of *A. nidulans* and its mode of perennation. Fig. 1. Long germ tube from the conidium creeping along the cuticle,  $\times 620$ . Fig. 2. Germ tube entering the cuticle,  $\times 780$ . Fig. 3. Infecting hypha taking a turn when comes near the epidermis,  $\times 620$ . Fig. 4. Subcuticular hypha,  $\times 620$ . Fig. 5. Conidium in the substomatal cavity,  $\times 780$ . Fig. 6. Hypha in *a.* substomatal cavity and *b.* the subcuticular region,  $\times 780$ . Figs. 7 and 8. Hyphae in *d.* ducts and *e.* a cell of the outer mesocarp of the fruits before removal for ripening.



the dead tissues produced due to the operation. A summary of the results is presented in Table VIII.

TABLE VIII

*The differential rotting when an equal amount of inoculum is put at different depths in the fruit*

Place of inoculum	Wt. of the fresh tissue used for inoculation in gm.	Wt. of the tissue 2 weeks after inoculation in gm.	Wt. of the diseased tissue in gm.	Average wt. of the diseased tissue in percentage
1. Under the green skin..	2936.5	2239.4	8.0	0.3
2. Depth of 5 mm. ..	2842.5	2265.6	166.4	7.3
3. Just above the stone ..	3410.4	2664.4	382.5	14.3

An examination showed that even allowing slight positional differences there was practically no rotting when the inoculum is introduced just below the green skin, the maximum being in cases where the inoculum reaches the stone. Thus in fruits of the first set only 8.0 gm. of the rotten tissue was obtained in 2239.4 gm. of the tissue used for inoculation. In the second and the third sets 7.3% and 14.3% of the diseased tissue was isolated respectively.

It, therefore, becomes clear that different tissues in the fruit show different degrees of resistance to the fungus and the amount of rot will depend on the depth the fungus is able to traverse before being picked for ripening. The resistance is highest near the epidermal region and decreases with the increase in depth. The epidermis and the outer mesocarp offer considerable resistance whereas the deeper tissues (middle and the inner mesocarp) are more susceptible, favouring the lateral spread of the fungus. If the fungus does not cross the limits of the green skin (outer mesocarp), it will only produce superficial lesions. In order that the fungus may produce the rot in the inner mesocarp, it must overcome the resistance of the external layers and then penetrate into the deeper tissues. Under low conditions of resistance the hyphæ penetrate the epidermis, grow into the outer mesocarp and involve its ducts and cells. This differential reaction of the tissues, thus is of considerable significance in storage. The amount of inoculum may also play an important part in initiating the rot in the living tissue, but a certain minimum number of hyphæ may be required for the purpose.

### DISCUSSION

Considerable amount of work has been done on latent infections both outside and in India. Shear and Wood (1913) found dormant infections of *Colletotrichum* and *Glomerella* in the leaves, stems, flowers and fruits of many plants. Dastur (1919) showed that *Glæosporium musarum* is present as latent infection in immature bananas. Wardlaw (1931) confirmed Dastur's observations. Wardlaw and Baker (1926)



demonstrated the presence of *Colletotrichum Glæosporioides* in green mangoes. Baker and Wardlaw (1937) have proved that several fungi are of common occurrence in the tissues of tropical fruits and by the time they are harvested they contain latent infections of several fungi. Baker (1938) made a survey of the organisms which may occur as latent infections during the development of the tropical fruits and drew a relation between the latent infecting fungi, the organisms present on the general surface of the fruits and in the orchard. Sinha (Unpublished) traced the origin of some of the diseases in storage to the infection in the orchard.

A comparative study of the number and the concentration of orchard fungi during various periods in the mango season yielded as many as 13 strains. Some of them (*Aspergillus nidulans* and *A. niger*) were present always, others like *Aspergillus* sp., *Penicillium* sp. and *Rhizopus arrhizus* occurred only occasionally. The relative concentrations of the strains were also found to vary with time but as the factors operating in an orchard are many and variable, it was not possible to draw any general conclusion. Baker (1938) obtained a considerable amount of saprophytic fungal flora in the grape fruit orchard and from the studies extending to nearly one year concluded that the modifying effect of the season on the constituent members of this flora is negligible.

Sinha (Unpublished) isolated only 5 fungi from the surface of mangoes stored in market. Surface washing of Khajli and Phajli fruits, gathered directly from the orchard, have given 9 fungi, some of them are common with those obtained by Sinha. *Neocosmospora vasinfecta* reported by Sinha was found to be absent in these mangoes.

Since the atmospheric flora differs from place to place, different latent fungi are expected under different conditions. Baker and Wardlaw (1937) and Baker (1938) obtained *Colletotrichum Glæosporioides*, *Phomopsis* sp., *Dothiorella ribis* and *Guignardia* sp. as latent infections in green mangoes. Sinha (Unpublished) could recover 4 strains under Lucknow conditions—*Colletotrichum capsici*, *Aspergillus nidulans*, and two sterile strains. In the present investigations five fungi, viz., *Aspergillus nidulans*, *A. niger*, *Fusarium* sp. 1, *Alternaria* sp. and *Acrothecium* sp., were obtained from the Khajli and Phajli varieties. The three fungi of relatively greater importance are *A. nidulans*, *A. niger* and *Fusarium*, *Fusarium* being mainly isolated from the unfertilised and fertilised ovaries. Baker (1938) explained the occurrence of *Fusarium* by the fact that it possesses resistant spores, sometimes capable of withstanding the surface sterilisation technique.

The superficial fungi and those obtained in the atmosphere of the orchard are found to be related to the latent infecting ones. The five fungi, recovered from the apparently healthy fruits, are in common with the 9 obtained as superficial isolates and the 13 collected from the orchard during various periods of the mango season.

Baker and Wardlaw (1937) and Baker (1938) showed latent infections in the fruits of all sizes and proved that in many instances these latent infections are established shortly after the fruits are set. Baker,



Crowdy and McKee (1940) stated that the young mango fruits are readily infected as compared to the old ones, the infection reaching the maximum intensity when the fruits are about half developed. The results of the investigations embodied here reveal that latent infections are definitely related to the age of the mango fruits. They are more susceptible to *A. nidulans* during the earlier stages. The older ones, either are incapable of being infected or are much more resistant. Even by spraying a concentrated suspension of spores of *A. nidulans* no appreciable increase in the latent infection has been found in the fruits of medium and large size. The maximum period of susceptibility lasts till the fruits are about 70–80 mm. in length. Experiments with the isolation of the fungus in question from apparently healthy fruits also support the above observations for the stage of isolation and the stage at which artificial infections are possible are more or less the same. Further, the observations indicate that the amount of infection is directly related to the concentration of the respective fungi on the surface of the fruits and in the atmosphere of the orchard provided the fruits are at the susceptible stage.

A certain amount of work has been done on the mode of perennation of the latent fungi and the histological changes associated with it. Kidd and Beaumont (1925), during the course of their study with storage diseases of apples, came across spores that remained on the general surface of the fruits and in the lenticels until such a time as they were able to germinate and enter the tissues. Horne and Palmer (1935) showed that *Dothiorella ribis* enters the young lenticels of immature avacado pears on trees and forms the mycelium which remains dormant in the air spaces until the fruit is becoming senescent in storage. The present investigations show that while in most cases the conidia are abundantly present and remain quite firmly lodged on the general surface of the fruits, in two preparations the conidia of *A. nidulans* and the hyphæ produced from them were found in the substomatal cavity. Of more common occurrence is a hypha of limited growth (presumed to be of *A. nidulans*) in the subcuticular region.

Regarding the mechanism and the nature of latent infection Wardlaw, Baker and Crowdy (1938) have shown the infection of papaw fruits through the stomata at any stage, at a temperature of 80°–90°, in a saturated or nearly saturated atmosphere. Baker, Crowdy and McKee (1940) showed that for successful infection of the mango fruit by *Colletotrichum Glæosporioides* and allied fungi, an initial period with relative humidity at or near the saturation point, was necessary and this period need not persist for more than 12 hours provided the fruits are not subjected to abnormally dry conditions. The conidia of *A. nidulans*, the fungus in the present study, germinate in a few hours and cause an entry in less than 24 hours. Though the spores are present on the general surface, around and on the lenticels and stomata, they pierce through the cuticle. The fungus, in the ordinary course, unlike *Botryodiplodia theobromæ* (Baker and Wardlaw 1937), is not a wound infecting one though its presence does ensure the entry. There is no structure comparable to the appressorium developed as is found in *Colletotrichum* (Dey, 1919 and Simmonds, 1941). The



entry of the fungus into the epidermal tissue by puncturing the cuticle probably explains the fact that latent infection occurs mostly during the early stage of the development of the fruits. It is probable that due to changes in the cuticle in more mature fruits the infected hyphæ are unable to puncture and gain an entry. The infecting hyphæ after making a puncture in the cuticle remain in a subcuticular position similar to *Colletotrichum* and *Glaeosporium* (Simmonds, 1941) and unlike *Colletotrichum lindemuthianum* (Dey, 1919) where the mycelium penetrates the cuticle and persists in the epidermal cells. The artificially infected fruits while on trees do not exhibit any anthracnose lesions but in the laboratory experiment, small orange coloured areas developed at places where the fungus made its entry.

The subcuticular hypha is believed to be the form in which the fungus survives the period of latency. It remains in a latent state for about two months and starts its spread just before the fruits are picked for storage.

The different tissues in the fruit show different degrees of resistance and the amount of rot will depend on the depth the fungus is able to traverse before being picked for ripening. If the focus of infection is deep down into the tissue (inner mesocarp) the greater will be the rot produced. The fungus must cross the limits of the green skin to produce its full pathogenic effects otherwise it will only produce superficial lesions not involving deeper tissues.

The absence of active parasitism during the earlier stages can be attributed to several factors either acting singly or in combination. Dastur (1919), Ghatak (1938) and Baker *et al.* (1940) maintain that the chemical constitution of the fruit is chiefly responsible for this behaviour. Simmonds (1941) who is more definite attributes it to the fact that the upper cellulose layer acts as a barrier which the parasite is unable to overcome owing to its chemical nature or the constitution of the cell-sap and the later advance is facilitated by the withdrawal of the toxic substances due to an increase in the enzyme action or by alterations in the cell-sap. The present investigations show that the innermost cuticular layer, which is characterised by its being denser and at times yellower, offers considerable resistance to the invading organism, thereby arresting its further advance, the degree of resistance determining the position taken by the subcuticular hypha—either directly above or even slightly raised above the epidermal cells. Later advance, which in most probability is brought about the time of picking, is initiated by the weakening of the lower tissues due to various physical and chemical changes associated with growth and senescence of the fruits.

#### SUMMARY

The paper deals with the investigations on the latent infection in the mango fruit using two varieties—Khajli and Phajli.

Thirteen fungi were found to occur in varying concentrations in the atmosphere of the orchard, of which nine strains were common with the fungi obtained from the general surface of the fruits. Some



of these have been noticed to occur throughout the mango season, some quite frequently and still others only rarely.

Five different fungi have been isolated as latent infections from the unfertilised ovary to the mature fruit before the time of picking. Some of these have been isolated more frequently than others. All the latent fungi are common to those found on the general surface of the fruit and in the orchard under natural conditions.

Two methods, viz., spray of a concentrated conidial suspension and an application of conidia on the superficial wounds have been used to cause latent infections artificially by *A. nidulans*.

Younger stages (below 75 mm.) are more susceptible, the resistance of the fruits increasing with the advancement in maturity.

Investigations include observations on the mode of perennation of the fungus during the period of latency. The conidia are abundantly present on the general fruit surface and some of these remain quite firmly lodged. Germinated and ungerminated conidia were also detected in the substomatal cavity. A more common method of perennation is a hypha of limited growth (presumed to be of *A. nidulans*) that remains dormant in the subcuticular region.

The hypha gains an entry into subcuticular region by piercing through the cuticle. The course of the infecting hypha has been demonstrated.

The subcuticular hypha remains dormant for about two months, till the fruits are on trees and it is believed that this hypha resumes its activity a little before the fruits are picked, and reaches its maximum when the fruits are in storage.

Different tissues of the fruit have been found to behave differently. The epidermis and the outer mesocarp offer considerable resistance to the organism whereas the deeper tissues are more susceptible favouring the lateral spread of the fungus. The amount of rot depends on the depth the fungus is able to traverse before being picked for ripening. If the fungus does not cross the limits of the green skin it will only produce superficial lesions.

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\* Not seen in originals.







34th INDIAN SCIENCE CONGRESS, DELHI, 1947  
SECTION OF PSYCHOLOGY AND EDUCATIONAL SCIENCE

PRESIDENT: PROF. P. S. NAIDU

*Presidential Address*

PSYCHOLOGY AND THE REHABILITATION OF HUMAN SOCIETY

I

THE MORASS OF THE PRESENT AND A WAY OUT

We are meeting at a most critical period in the history of the human race. Compared with the magnitude of the disaster which is threatening the world today the crises in the past history of man pale into insignificance. And the prevailing gloom deepens immeasurably in the minds of many of us as we glance back and recall the exuberant optimism which filled our lives in the not distant past. To those of us who were studying in the Colleges and Universities in the second decade of this century the alluring vista that opened out before us was 'one of advancing civilisation, of peace seldom broken and of knowledge everywhere expanding.' And we were about to lull ourselves into comfortable sleep to the ravishing tunes of what we believed to have been the marching song of humanity joyously striding on to peace and prosperity. CAME THE CRASH!—the first world war administering a rude shock to our self complacency. We were forced to witness the hideous spectacles of this fair and smiling earth of ours turned into a dreadful inferno by,

'Clanging fists, and flaming towns,  
And sinking ships and preying hands.'

The battle fields were never before so hideous, and the atrocities committed thereon so inhuman as in 1914 to 1918. Man's sense of decency was outraged, and his faith in himself was uprooted. These frightful events together with the severe economic depression that followed, we thought, were enough to produce a sobering effect on the turbulent elements in man's nature. But we were sadly disappointed. The war which we thought was being fought to end all wars only ended in sowing the seeds of another and a more inhuman war which has made all of us victims to untold loss and suffering. And this war was brought to an end dramatically by the use of weapon so ruthless, so indiscriminating in its destructive results, and foreshadowing such terrible consequences for the future that its own authors stand appalled. In the midst of all this gloom and despair we are constrained to exclaim,

..... Ah! man, proud man,  
like an angry ape  
Plays such fantastic tricks before high heaven  
As make angels weep!."

And we grow rigid with terror when we are told that a third global war is in the offing!

"It is not the phenomenon of war as such that is disquieting, but the regularity and frequency with which humanity is seized with this fratricidal mania. It is not as though the sadistic lusts and barbaric passions unleashed by war marred the pages of history here and there so that they may be passed



by without comment. The human race seems to indulge in these unholy orgies periodically, and the advance of civilisation seems but to refine the means by which nations slake their thirst for the blood of brother nations. The perusal of general history unfolds a gloomy tale of the insensate greeds, lusts and panic fears, and of the ferocious passions and hideous deeds of the uncultured mass."<sup>1</sup> How true this observation is of contemporary history may be seen if we peruse the records of the International War Crimes Tribunal. Sir Hartley Shawcross who prosecuted the war criminals in Europe denounces the top-ranking men who organised the inhuman tortures as no better than common murderers who were morally guilty of crimes so frightful that imagination staggers back. Justice Jackson remarks with infinite sadness in his heart that these crimes which offended against the sanctity of human personality, this mad and melancholy record, would live in history as the text of twentieth century's shame and depravity. But, let it be noted that this shame and this depravity of the present 'civilised' century are not confined to any one country, nor even to the battle field. We had a first hand experience of 'the bestiality and brutality of the uncultured mass of the twentieth century' in the recent riots nearer home on either side of us, and that too in peace time! The slightest irritant seems to induce man to slough off his thin and loosely fitting skin of civilisation and display himself shamelessly in all his brutal and primitive nakedness. It may have been fondly believed by a few that man was made in the likeness of his Creator and placed but a little lower than the angels, but history seems to point to the Darwinian conception of man's origin as the nearer approach to truth. **MAN IS TRULY AN INSTINCTIVE ANIMAL.** And the angels may well go into tears to see this sorry parody of the Divine Creator's benevolent aim and purpose!

What then is the remedy? Or is there no remedy at all? Have centuries of culture and civilisation proved utterly ineffective? Have all the efforts of man to rescue himself from the clutches of the brute in him been in vain? Is there then no hope for man? Is he doomed to perish, and be wiped off the face of the earth? **NO, HE IS NOT CONDEMNED TO SUCH A SORRY DOOM.** I for one have no hesitation in saying that there is hope for man yet. *And that hope comes from PSYCHOLOGY.* In my own mind that hope is born of a deep and abiding faith in the high destiny to which psychology is called today. It is my passionate desire to carry all of you with me, my anxiety to infect you as it were with my optimism in regard to the competence of psychology to recondition human nature, it is this deep seated longing that prompted me, Sir, to choose 'Psychology and the Rehabilitation of Human Society' as the theme of my address when, out of their kindness and generosity, my respected colleagues on the Sectional Committee conferred on me the high honour of Presidentship of the Section, and the Executive Committee and the General Committee of the Science Congress also considered me worthy of that honour. I am deeply grateful to all of them, and trust that I shall be able to fulfil worthily the duties entrusted to me.

Speaking psychologically, and philosophically too for that matter, self-knowledge, self-discipline and self-control are the main ingredients of the potion that modern man must quaff in order to rid himself of the disease that is torturing his body, mind and soul. In days gone by these ingredients were provided by spiritual discipline which kept the intractable elements in human nature under proper control. True, it was only intuitive or mystical knowledge that they of ancient times had, but it was enough to keep man from

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1. Naidu, P. S. *The Historic Process* (Meller Lectures, Madras University), 1946.



mischievous. Then came science in the fullness of time, and destroyed spirituality and mysticism, but put nothing in their stead. The rudder has been broken, the ballast thrown overboard, while the winds on the sails are being blown into ferocious violence. The vessel is heading towards the rocks, and something must be done and done at once to save man from disaster. One obvious solution lies in going back to the discipline of the ancients, but to the minds of men and women steeped in the realistic and materialistic spirit of science this will be unpalatable. To them a scientific solution alone will make a ready appeal. I do not agree with those who denounce science, and say that science should take a holiday. Let us by all means have science, more science, and still more science—but (and it is a very big BUT)—*the right type of science.*

## IT IS HERE THAT THE SCIENCE OF MAN COMES IN

### THE PROBLEM OF SCIENCE AND SOCIETY—A BRIEF HISTORICAL SKETCH

It is an encouraging sign of the times that in our own country as well as in foreign lands scientists are steadily realising the need for a re-orientation of the values of science. They have begun to speak of the social functions of science, and to assess scientific achievement in terms of human values. There is now a feeling that it is not the group of sciences engrossed in the study of the physical environment, not even the group concerned with the biological environment, but the group attempting to delve into man, his mind and his social relations that should receive our most anxious care and consideration. This is no doubt a vague groping after the truth, but it is valuable as an index of the growing dissatisfaction in learned circles with the exaltation of sub-human values which inspired the scientific workers of the previous centuries. A rapid aerial survey of the history of this new movement in science will reveal whither exactly it is tending, and the points where it is going astray. Let me attempt the survey.

It was in the year 1927 that the scientists who met at Leeds under the auspices of the British Association for the Advancement of Science were rudely awakened from their slumber by a striking sermon which was preached to them by the Bishop of Ripon. In spite of all his new mastery of nature, the Bishop said, man did not seem to be really advancing his own cause. Development of his resources did not spell either development or happiness for himself. And the Bishop asserted with all the emphasis at his command, 'that the sense of direction had been lost amidst all the new discoveries'. Unless parallel progress was being made towards moral and spiritual supremacy could we dare to go on, asked the learned divine, enhancing man's bodily values without some sure hope of saving his soul? These exalted sentiments uttered by the Bishop made a deep impression on the scientists. In 1932 President Ewing asked of the assembled gathering of British scientists, 'Whither does this tremendous procession of science tend? What, after all, is its goal? What is its probable influence upon the future of the human race?' And the president declared that 'the command of nature had been put into man's hands before he knew how to command himself.' A very significant event occurred at this gathering. Prof. Hopkins pointed out that apart from war, *science and invention had done little to increase opportunities for draining off the more serious of man's irrational impulses.* Without intending to do so consciously, the professor touched the profound psychological problem of canalising the energy of the unsocial complexes in the unconscious layer of the human mind. The next important event is the presidential



address of Josiah Stamp delivered in 1936. Stamp spoke of the impact of science on society, and for the first time came out boldly with the suggestion that the increasing difficulties confronting human society might be reduced by psychological research which would reveal the laws governing human behaviour. He declared that more money should be spent in biological and *psychological research*, as at the time he was speaking the expenditure on the social sciences was only a tenth of what was spent on the natural sciences. The year 1936 also saw another notable event in the history of science. Among the delegates to that year's session of the British Association were E. G. Conklin, the President of the American Association for the Advancement of Science, and a group of distinguished American scientists who were much impressed by the frank discussion of the social relations of science. They decided to cooperate with the British Association in advancing the study of the social bearings of science and in promoting peace and intellectual freedom. About this time the Royal Society in England and the National Academy of Sciences in the United States of America organised exchange lectureships for the study of the progress of science, and of ideas that give promise of happiness for mankind. And all these forces, though operating from different points and on different planes, led to the formation in 1938 of a new division of the British Association, the division for the study of the 'social and international relations of science.' This division is pregnant with great promise for the future, and if it will only press into its service the findings of contemporary psychology it will prove to be a great force for securing human happiness.<sup>2</sup>

In our own country the movement for the socialisation of science is of very recent origin. It is yet in its infancy as is proved by the fact that we do not have a separate division for the study of the social bearings of science. It was in 1938, the year made conspicuous in the history of science in England by the establishment of an independent section for studying the human implications of science and invention, that the Indian Science Congress took the first step towards the establishment of an organisation for investigating this new problem. In 1940 a sub-committee was appointed to study the impact of science on Indian society. During the years that followed, despite the devastating effects of the world war, the sub-committee made striking progress towards the fulfilment of the task entrusted to its care. A significant feature of the work of the sub-committee was the series of lectures delivered in 1944 by Dr. Kewal Motwani at different university centres in our country. A determined effort is being made to evaluate correctly the progress, interconnections and directions of advance in the physical, biological and social sciences, and to tackle the question of lag in the application of scientific knowledge to the life of the people in India. Recently it has been laid down that one of the major objectives of the sub-committee should be 'to make society more appreciative of the achievements of science and to focus public attention on the social applications of science.'

### The Pressing Need of the Moment—DEPTH PSYCHOLOGY

All this is quite impressive and exhilarating to the student of the social sciences, but it does not seem to have been productive of any tangible result. The report of our sub-committee for 1945 ends with a pessimistic note. The reason for this is not far to seek. Both in our country and in England only the outermost fringes of the difficult problem of science and its influence on the deeper nature of man have been touched. The *psychological forces*

2. Crowther, J. G. *The Social Relations of Science* (London 1941), pp. 612 f.



which lie at the heart of man have been ignored. And where psychology is mentioned at all, the reference is just superficial enough to make it either useless or dangerous. No attempt has been made by these committees to dive deep into the mind of man to uncover the secret springs of his tantalising behaviour. Without a firm grasp of the psychological principles, no problem relating to the impact of science on society can be solved, and no scheme for the rehabilitation of human society can be fruitful. To psychology, then, every student of the social sciences must turn for guidance and help.

Permit me to make a slight digression at this stage. Large hearted and intellectually gifted men and women of all countries who have noted with infinite pain and sadness the steady degradation of human nature in the face of 'advancing civilisation' have sought anxiously to locate the cause for this fall of man. And they think that they see the root of the trouble in the unequal development of man's intellectual and moral nature. It is Professor Einstein, I believe, who spoke of the lag between the achievements of man's brain and the deeper promptings of his heart. A political thinker of standing remarks that 'in the course of a few generations human beings have learned to control physical forces without acquiring a like measure of control over themselves and their relations to one another.' We agree to these conclusions, but we go farther than these thinkers and demand an explanation for the lag between the achievements of the cognitive and conative aspects of the human mind. The scientists however, are unable to meet our demand because of their obsession with the external environment, with the outer and less important conditions of human behaviour. The belief persists among all, scientists not excepted, that by reshuffling the environment human nature may somehow be improved. It is not seen that without an understanding of the psychological forces governing human behaviour, it will be utterly futile to plan for the improvement of human society. *The findings of Applied, Experimental and Depth sections of Psychology should be accorded the place of prime importance in all plans for the future ordering of human society.*

#### THE COVERT CAUSE FOR THE OVERT NEGLECT OF DEPTH PSYCHOLOGY

That all programmes for reorganising human society should be broad based on sound psychological principles is a trite saying. Yet, what do we witness in the world of science today? Men gifted with keen understanding have failed to grasp this simple truth. Their recognition of psychology is grudgingly given. Our Science Congress is a notable exception: elsewhere there is total neglect of this fundamental science of man. One reason for this neglect is that modern society is inclined to ignore the individual. It takes into account only what it calls *the social whole*. It believes that the universal is the real existent while the individual is only an abstraction, and this confusion has led to the relegation of man, and the science of man to the distant background. This error, serious as it is, may be set right by the proper education of society. But there is another and a more subtle cause for the neglect of psychology, and this has its origin in the powerful and dynamic motives rooted in the unconscious. The mere study of psychology and other social sciences will lead to an unsparing criticism of the present social institutions. The true science of man will expose, as psycho-analysis has exposed, the hollow pretensions and the folly of modern civilisation based on an obsessive preoccupation with the outer environment to the utter exclusion of the inner nature of man. No wonder, then that depth psychology and its leaders are hated and reviled. Advances in the physical and biologi-



cal sciences serve but to gratify man's craving for self indulgence, while advance in depth psychology will lift the gossamer veil covering human nature, and will expose the shell within rattling with ugly and repulsive primitive instincts. Depth psychology will demand self-control, self-discipline and renunciation of the objects of sense enjoyment. The hostility to psychology is a defence mechanism. The resistance is deep seated and is not easily handled by one who is not in possession of the secrets of the unconscious. Psychology is viewed by many as a mischievously tendentious science. Let us not fall victims to this spirit which is spreading steadily from the West and the North to engulf our land. With our age long training in fearless introspective analysis, we in this country should easily arrest the tide of environmentalism that is sweeping on us from the North. We in this country should have no hesitation in according to the science of man the sovereign place that is its due.

## II

### THE PSYCHOLOGICAL OBJECTIVES OF OUR PLANS

When we press psychology into service in our endeavours to plan for the future of human society, we find that this science prescribes a hierarchy of three goals as worthy of pursuit by us. They are EFFICIENCY, HAPPINESS and SELF-REALISATION. *Efficiency* relates to the body and the superficial levels of the mind, *happiness* to the deeper mental levels and *self-realisation* to the total personality, to the whole being of man. Psychology does not stop with the mere dictation of aims. If it did it would be unworthy of our allegiance. It prescribes also the means by which the goals may be reached, and the methods by which human society may be rehabilitated. To experimental psychology and applied psychology we have to look for help to attain *efficiency, the lowest goal* in the three-fold hierarchy, to depth psychology for the attainment of *happiness the middle goal*, and to spiritual psychology, the unique contribution of our country, for the realisation of *the highest goal of self-realisation*. No scheme for the rehabilitation of human society will have any chance of success which neglects any one of the components of this three-fold hierarchy. Let us turn to the three leading branches of psychology mentioned above for guidance in drawing up the outlines of a plan for the welfare of mankind.

### Square Pegs in Round Holes!

#### FIRST COMES APPLIED PSYCHOLOGY

It is now a well established fact that a great deal of avoidable misery and pain in human society is caused by the wrong placement of personnel in the services and the professions. The wrong pegs are in the wrong holes, and this maladjustment in life is a lasting source of wastage and suffering. Our energy, whether mental or physical, is strictly limited in amount and at any given moment the amount available is also limited. How best may this energy be used? That is an important psychological question, and on the answer to it depends the success or failure of all industrial plans. For each man there is one and only one best way of doing things. The determination of this best way is the task of applied psychology, and it is this best way that I have spoken of as the goal of *efficiency*, which is none other than the attainment of perfect balance and harmony between the innate psychological abilities, talents and temperament of the worker and the job at which he has to work for the greater part of his life. There is at the present moment



a lamentable neglect of the psychological factor on the part of those who are responsible for selecting personnel. 'The raw materials for industry are generally subjected to the most rigorous tests in the firm's laboratory before they are accepted. . . . the claims of rival firms of machinery-makers are closely studied by skilled engineers before even a small piece of new plant is bought. But the choice of the staff—surely the life of the business—is often left to an unskilled minor executive who has no special competence or knowledge.'<sup>3</sup> Prof. C. S. Myers says, 'It is extraordinarily common to find the human factor ignored when mechanical improvements are introduced, or insufficiently considered when attempts are made to deal with it.' The indifference displayed by all concerned in the matter of the psychological handling of man-power has resulted in serious economic loss and in widespread discontent and mental unbalancing. Enormous labour turn-over is the first unfortunate result of the prevailing unpsychological methods of organising man-power. It may come as a surprise to many of us that the loss in England alone due to unpsychological methods of recruiting industrial labour is one hundred million pounds every year! Apart from this huge financial loss we know how the present slipshod method of fixing square pegs in round holes and round pegs in square holes is in many instances responsible for delinquency and even for certain types of insanity. And we should not ignore the possibility of finding a potent cause for the present labour unrest and mass hysteria in the unscientific methods of recruitment. What then is the remedy? Human Engineering on sound psychological principles is the only remedy that is indicated as the pressing need of the hour by a correct diagnosis of the symptoms of our social disease.

## AND IT IS HERE THAT APPLIED PSYCHOLOGY COMES IN.

### A PSYCHOLOGICAL PLAN FOR INDUSTRIAL EFFICIENCY

I now proceed to suggest a plan<sup>4</sup> for achieving *efficiency* in our national life. The first step that I would prescribe for an efficient, fruitful and scientific rehabilitation of our national life is an extensive nation-wide survey of the abilities of our boys and girls of all ages and all grades who are now at school. The testing should be done at the time of admitting a child into the lowest elementary school grade. In fact, it should be done even earlier, and when infant schools become a regular feature of our educational organisation, this testing should be done at the earliest infant school stage. And, thereafter re-testing should be carried out regularly every year. Along with the medical inspection of the children, the testing of intelligence also should be carried out. In fact the medical inspection chart should have in it a section set apart for recording the results of mental tests.

The tools required for this extensive psychological survey of national intelligence are ready to hand, but like other imported wares they require reconditioning to suit local requirements. Fruitful work is being done in an isolated and uncoordinated manner at many centres in our country. What is urgently needed is the coordination of all this valuable work under the guidance of a central Psychological Research Organisation with a view to evolve standardised tests in the various provincial languages. These tests will then be the most reliable tools for the survey mentioned above.

The second step in the plan for the scientific ordering of our national life consists in applying vocational tests or tests of special ability for discovering

3. Myers, C. S. *Industrial Psychology*.

4. Naidu, P. S. "*Utilisation of Indian Man-Power*", (Bombay, 1945).



the innate specific capacities of children of school-going age. Along with the general intelligence test, the tests for special abilities should be administered commencing from the middle school stage. The latent abilities and aptitudes of boys and girls at this stage of their school career should be discovered, and thereafter through regular annual retesting a careful and anxious watch should be kept on the way this latent ability gradually unfolds itself. Then, at the high school or the polytechnic stage steps should be taken to train and develop the latent capacity according to strict psychological methods.

After the survey of general intelligence and of special abilities comes another important stage in our plan. Contemporary psychology teaches us that a man's temperament and his social and moral qualities should also be taken into consideration in assigning him to a particular job. The point that I am stressing has been hit off most happily by Prof. Cattell. 'There are people' says this learned psychologist 'who would prefer to earn a living by putting dots on dice, and others who would be happier 'earning' a living by throwing the dice!'

A complete survey of human personality in all its myriad tantalising forms is a Herculean task, but luckily for us the significant traits appear to be only a few and easily manageable. These should be treated psychologically and pressed into the service of our plan.

The data gathered so far from a psychological investigation of general intelligence, special abilities, talents and temperament of the testees should be subjected to the most up-to-date statistical treatment, and the profile drawn for the individual testee. And then arises the final problem of finding the job just suited to the individual concerned. This leads us on to job analysis. So, as the next step in our plan we recommend that the various vocations, arts and professions be treated psychologically, and analysed with a view to discover the demands which they will make on the cognitive and conative abilities of the workers. Job profiles corresponding to the testee profiles have to be carefully prepared. When this task is completed, then it becomes an easy matter to fit the individual to the job best suited to him. Let us remind ourselves of the very valuable lesson that scientific psychology has taught us, namely, that *each man is a genius at something*. It is the duty of the industrial planner to discover what that something is. When that discovery has been made, and the steps outlined above taken to make the discovery effective in daily life, then we shall have attained the goal of efficiency in our three-fold hierarchy.

#### THE ORGANISATION OF AN ALL INDIA PSYCHOLOGICAL SERVICE

The machinery for the extensive psychological survey outlined above has to be created in our country. In the first place an Indian Institute of Industrial and Applied Psychology should be brought into existence at once. This body will concern itself with the framing and standardisation of tests. In the second place A Psychological Survey similar to the Indian Archaeological Survey or Zoological Survey should be organised. This body will conduct the actual field work in human engineering. The teachers and the medical inspectors attached to schools will have to do a good deal of the mechanical part of the work in administering the tests, but the responsibility for the technical direction will have to rest with the Indian Psychological Survey.

Finally, a National Council of Psychology composed of psychologists, leaders of commerce and industry, and other officials and non-officials should



be created. It is through this body that employers of labour and the psychological engineers will be brought into contact. They will, between them, settle questions of general policy, and will stimulate each other into such clearer modes of thinking as will lead to the attainment of efficiency, to the placing of right pegs in the right holes and to the elimination of avoidable wastage, pain and misery in human society.

### III

#### THE NEED FOR DEPTH PSYCHOLOGY

Efficiency, however, is only one of our goals. In fact it is the lowest goal. Had man been all body and with no soul, subject only to mechanistic and deterministic laws, then efficiency by itself would have afforded him complete satisfaction. Today, countries whose political ideologies are dominated by materialism, determinism and behaviourism are seeking only this goal of lesser value. We in our country with a hoary spiritual tradition will not and cannot be satisfied with mere robot-like efficiency. We have never lost sight of the fact that man is body mind and soul, and that in any scheme of national rehabilitation, therefore, we should aim at the attainment of the higher values of life. How are we to set about the realisation of these values?

#### IT IS HERE THAT DEPTH PSYCHOLOGY COMES IN

The programme that I have sketched above for the rehabilitation of our society is confined to the outer layers of the human mind: the deep lying core has not been touched as yet. Maladjustment in trade or profession is not the only cause for our social ills today. There are other causes, irrepressibly dynamic, operating from the ugly depths of the unconscious in the human mind. Often they assume the most impenetrable disguises. We must penetrate into the deep-lying, forbidding caverns of the human mind and cleanse the augean rubbish that has accumulated there. We must ruthlessly apply the lancet supplied to us by depth psychology, and drain the suppurating ulcers in the unconscious.

#### THE ALARMING SPREAD OF INSANITY IN CONTEMPORARY LIFE

To the impartial student of psychology making an objective survey of the human situation today it is brought home with irresistible conviction that there is a steady spread of insanity in the human mind. Wars, political squabbles, labour strikes and lock-outs, and other fissaiparous forces are disrupting national and international relationships. Divorce, suicide, crime and gangsterism are alarmingly on the increase. Neurasthenia, hysteria, anxiety neuroses, phobias and obsessions of myriad forms have gained ascendancy over the human mind. And even those who have managed to keep on the outermost fringes of the whirlpool of contemporary world conflicts have not escaped the ravages of neuroses. Like the common cold and minor digestive disorders, mild-neurosis is universally prevalent. For the attainment of true happiness these mental ailments should be banished, and for banishing them there must be on our part a frank and fearless recognition of their true nature and of their origin in the depths of the unconscious. Let me give a quotation or two in support of my proposition. That investigator with penetrating psychological insight, Dr. Schmalhausen says in his book *Why We Misbehave*, 'Whether we go over the field of criminology, juvenile



delinquency, marriage and divorce, business relations, the institutions of the home, the church, the state, the school, or study the intricate taboos and sanctions of ethical codes or peer into the intricacies of journalism, or specialise in the phenomena of crowd behaviour, persistently and inseparably we are in the perturbing presence of problems that can only be approached intelligently from a psychiatric point of view. *History penetratingly conceived is a branch of psychoanalytic psychiatry.* Again, one of my learned predecessors in this presidential chair Dr. Latif, has shown convincingly that 'the key to the social and political turmoil of any country is to be found in the psychopathology of the young anarchists.' The learned Doctor, in his presidential address to this section delivered in 1941, says 'Psychoanalytic study' has demonstrated that oftener than not . . . . the anarchists have been recruited from the ranks of the victims of a deep unconscious hatred against parental authority. Their revolt against political authority was a substitute reaction. . . . Such individuals have been the victims of uncongenial family situations during their early childhood in which the male parent, unwittingly or otherwise, provoked the growing boy to harbour feelings of resentment and retaliation, feelings which he subsequently projects on to objects, which even in the remotest degree serve to remind him of parental autocracy. . . . Thus . . . . an anarchist displaces his hatred for his father or father-substitutes on to social and political authority, and makes the world responsible for his unhappy childhood. A great deal of anti-social behaviour is found to be in the last analysis the result of displacement from the family to social maladjustment.' What has been said of the anarchist is true in a greater or lesser measure of every one of us afflicted with unhappiness. It is clear, therefore, that no attempt at making man happy, or at the rehabilitation of human society, will bear any fruit unless we cease dabbling in the science of man, and take seriously to the study of the deeper foundations of the science; unless we cease our irresponsible sport with the superficial conscious levels of the human mind to dive deep into its mysterious depths of the unconscious.

#### EVOLUTION OF THE INSTINCTUAL STRUCTURE OF THE HUMAN MIND

It is one of the irrefutable findings of depth psychology that 'man is as much driven by his instincts as any other creature, and that the function of intelligence—by which he was to be distinguished from the brutes—is to serve him in the following up of his instinctual needs.' I have said already that *man is fully and truly defined as an instinctual animal.* In an oft quoted passage the leader of Hormic Psychology says, 'Take away these instinctive dispositions with their powerful impulses and the organism would become incapable of activity of any kind. It would lie inert and motionless like a wonderful clock whose main-spring had been removed or a steam engine whose fires had been drawn. These impulses are the mental forces that maintain and shape all the life of individuals and societies, and in them we are confronted with the central mystery of life and mind and will.'

In the face of the formidable array of facts marshalled by depth psychology it will be utterly futile to deny that man's mind is merely a bundle of instincts. There is nothing more and nothing less than these primitive impulses in the structure of the human mind. As we have to solve the very practical problem of how to bring happiness to the doors of afflicted humanity, we need to know the origin and the course of development of our instinctual nature. Phylogenetic and ontogenetic studies carried out on the psychological level have revealed to us the secrets of mental evolution which had puzzled the old-time arm chair psychologists. The primordial undifferen-



tiated homogeneous instinctual matrix, call it *horme*, the *elan vital*, *libido* or what you will, the bed-rock of the life of the organisms, first differentiates, in the course of its evolution, into a positive and a negative impulse, the former tending towards the maintenance and continuation of the individuation of the organism and the latter to the subordination and even the sacrifice of the individual to the group. The sex, aggressive and death instincts, as well as those relating to alimentation now begin to appear. Psychoanalysis and other allied schools of depth psychology have painted for us a striking picture of the dynamics of mental evolution at the lower levels in the unconscious depths of the mind. We are familiar with the manner of working of the forces of inhibition, regression, projection and transformation at this level. But between the levels conceived by Freud and those with which McDougall starts there is a vast abysmal gulf shrouded in thick darkness and mystery. Elsewhere<sup>5</sup> I have made an attempt to bridge this gaping chasm in our knowledge of the history of mental evolution. But I must confess to the highly speculative nature of my hypothesis. Here is an unexplored region awaiting a daring band of pioneers who will blazon the path for us to follow.

It will need the cooperative efforts of depth psychologists, comparative psychologists and field anthropologists and archeologists to break through this dense impenetrable jungle of the human mind, but when the region is penetrated it will undoubtedly yield up its secrets.

I would invite you to conceive of the upward surge of our life energy in the Bergsonian manner as the shooting up of a multi-explosive rocket which generates other equally multi-explosive projectiles at each detonation. Psychoanalysis takes us up to a certain point in our efforts to follow this impressive and complicated development of the human mind through the regions of the unconscious. But soon we lose sight of our rocket as it plunges into the murky regions of impenetrable gloom that I have mentioned above. And as it emerges again into light on the threshold of consciousness, the leader of Hormic psychology is ready there to receive and guide us. It is easy, speaking comparatively, to trace the evolution of mental structure and function from the instinctual levels conceived by McDougall right up to the highest cultural levels attained by man. The human mind, let it be remembered, is structured at the start of the course of its development, but not completely structured. This inherited structure was originally described by McDougall in terms of his set of instincts, but later in his career the leader of hormism spoke of propensities instead of instincts. 'A propensity is a disposition, a functional unit of the mind's total organisation, and it is one which, when it is excited, generates an active tendency, a striving, an impulse or drive towards some goal.' An innate propensity functions always in conjunction with an innate ability, and every ability has two aspects—the perceptive and the executive ; cognitive and motor. Of the innate propensities man has a certain number, about seventeen according to our author. These are (1) food-seeking, (2) disgust, (3) sex, (4) fear, (5) curiosity, (6) protective or parental, (7) gregarious, (8) self-assertive, (9) submissive, (10) anger, (11) appeal, (12) constructive, (13) acquisitive, (14) laughter, (15) comfort, (16) rest or sleep and (17) migratory propensities. A group of very simple propensities subserving bodily needs, such as coughing, sneezing, and breathing should be added.<sup>6</sup>

When a propensity is excited by the stimulation of its perceptive ability and is linked to certain innate executive abilities, it is accompanied by a definite and appreciable feeling. The subjective aspect of this experience is

5. Naidu, P. S. *The Hormie Theory* (In Print, Allahabad).

6. McDougall, W. *The Energies of Men*.



what has been called an emotion. Innate propensities, innate abilities and their conative affects are the units of mental structure. They are inherited and constitute the raw material of the edifice of life. Starting with this material man builds up the complicated patterns of behaviour which make or mar his own future life and the lives of his fellow beings.

The human mind, be it noted, is dynamic. In the course of its development the loose structure that is inherited is very considerably modified and re-patterned. The elementary units are so many centres of force and many of them are antagonistic to one another. In the course of mental evolution a few may dominate over the rest, or two or three elements may combine to produce a harmonious pattern. The primary mental elements thus get organised round men and objects into concrete sentiments. A little later, abstract sentiments come into existence. And on goes the human mind along the path of its development forming innumerable sentiments of the concrete and abstract types. These sentiments constantly come into conflict with one another, and very soon it becomes necessary to resolve the conflict by creating a hierarchy of sentiments. A graded scale of sentiment-values has to be organised by each individual for himself, and the master-sentiment or the supreme or sovereign sentiment in relation to which the grading is made will determine the *weltanschauung* for the individual. This sentiment-building is then the psychological process by which culture, individual or racial, comes into existence. And it is here that we must look for the secret of *happiness*, the middle goal in our hierarchy of values.

#### THE SECRET OF HAPPINESS AND THE WRONG APPROACH TO IT

Happiness is to be attained by the attainment of a harmoniously organised and integrated personality, or by the attainment of a fully sublimated psyche free from repressions and inhibitions. Speaking in terms of the evolutionary picture I have painted, happiness consists in the organisation of a proper scale of sentiment values where the energy of each lower centre of force is properly controlled and canalised by the dominating influence of the master-sentiment. And it may appear at first sight that the institutions which mankind have laboured hard through ages to bring into existence suffice for the attainment of our goal. Our educational, legal, political, professional, economic and other organisations should have sufficed for making some approximation to happiness. But they have not. They have failed woefully. And the reason is the mishandling of human nature through ignorance of human psychology. There is a peculiarity of the process of mental evolution which I have described that merits our attention. The nature of our mind is such that it must express itself outwardly in some visible form at each stage of evolution. For the ordinary man his daily conduct at home, in the place of business, in his club or on the play-ground is enough and satisfying as an expression of his mental culture. But for the great mind whose cultural level is very high the ordinary channels of expression are inadequate. It is then that the gifted individual creates for himself absolutely new channels of expression. He turns into a creative artist or an outstanding leader of political, social or religious reform. Works of art hitherto unknown, and human institutions and organisations hitherto undreamt of are brought into existence. Because these expressions of mental culture are carved out of the environment, it is wrongly believed that by merely manipulating, reshuffling or repatterning the environment the internal structure of the mind can also be reshaped and improved. So, all kinds of plans for the reform of education, for social uplift, and for economic and industrial reorganisation are being made in the hope



that by re-moulding the outer environment happiness will somehow be attained. I do not brand these plans as utterly worthless ; I do not for a moment intend to deny the possibility of attaining inner happiness through the proper ordering of our environment. But I do stress this: that for such ordering to be effective we must have very thorough knowledge of the laws which govern the relation between the dynamic psychological forces in the mind, and the effects which the mind produces in the environment. In particular, we must have deep insight into the manner in which the unconscious interposes itself between the conscious motives and plans of man and the final execution of these plans. Armed with this knowledge one may attack boldly the problems that face us today, but in the absence of such knowledge even the most profound understanding of the principles of economics, politics and non-psychological sociology will be of little avail.

### THE PSYCHOLOGICAL FORCES PULLING THE STRINGS OF DIALECTICAL MATERIALISM

Let me illustrate my point from a region of experimentation in human happiness which has dazzled the world by its apparent success.<sup>7</sup> Dialectical materialism has been made the basis for the ordering of society anew along certain novel lines. It is claimed that perfect happiness may be attained by complete subservience to this new ideology. But already the vision which inspired the founders of this new type of state regimentation at the cost of individual liberty is proving to be a mirage. I for one will not be surprised if it turns in the long run into a shameless Siren or Circe. The reason for this delusion is hidden deep in the unconscious of the leaders of communistic ideology. To understand the true nature of this force we must get back to the most primitive animistic or animatistic stages of man's existence. In the case of some notable individuals we find these stages recapitulated on the ideological level in their early lives. We find here a kind of crude monism which yet displays the rudiments of dualism in the form of indeterministic and spiritualistic idealism opposed to mechanistic and deterministic materialism. The former element which communistic ideology seeks sedulously to discard is really innate and may be traced to pre-natal or intra-uterine omnipotence of the individual. Repression consequent on frustration soon sets in and may perhaps be traced also to the pre-natal stage. However, in the post-natal stage the conflict soon arises between the egoistic instinctual impulses and the reality of the environment, particularly of the social environment. Repression becomes necessary and is to a large extent effective. And those of us who are familiar with the dynamics of the unconscious know how repression is often accompanied by projection. Some part of the innate indeterminism or intra-uterine omnipotence is handed over to the environment and a comfortable doctrine giving first priority to matter is formulated. This yields great comfort for, after the manner of infants and primitive men the responsibility for the frustration of selfish desires, and for the inability to cope with reality may be thrust now on to the environment. Further repressive action passes through a succession of developing phases, and eventually blossoms forth first in dualistic ideology in the indeterministic world of spirit or mind as separated from the deterministic world of matter, and the former is wholly repressed from consciousness leaving the ground free for mechanistic and materialistic ideology. But we know how repression generates an obsessive symptom which shows up the innate strength of the repressed impulse working unrecognised at the unconscious levels. The symptom in the case we are

7. *Atomics*, S. S. A. New Age Series, 1, p. 10 f.



considering is the violence of anti-god and anti-religious propaganda carried on with the tirelessness of a compulsive and repetitive neurosis. But this is not in any sense the end of the story. What is happening just now in the communistic country is just what we should expect to happen on the basis of our psychoanalytic interpretation of the history of dialectical materialism. Mechanistic ideology is only a half-way house in the evolution of the gorup mind under the control of the repressive process. At the next stage, when that country is involved in another whirlpool, there will be a weakening of the frustration-cum-repression dominance, and a gradual emergence into consciousness of the repressed element. This will be a most troublesome stage and will require very delicate handling with precision tools created by depth psychology. All the plans in operation just now in that country will be severely tested at that stage. I should like to mention at this stage what is self-evident to every student of psychoanalysis. Economic wants and economic motives are merely disguised and repressed erotic wishes. Wealth or money possesses erotic significance derived mostly from the anal stage of libidinous development. How then can any one hope to plan for happiness by reshuffling the economic structure of society who does not have a firm grasp of the psychological forces which control the economic life of man?

#### EFFECTIVE PSYCHOLOGICAL PLANNING FOR HAPPINESS

We have seen the course of mental evolution at the conscious as well as unconscious levels, and have noted that the springs which move the conscious are hidden in the unconscious. Any scheme for bringing happiness to the doors of man must take into account the psychological forces that operate both above and below the threshold of consciousness. The many plans that are now being made for economic and industrial reorganisation, for the reform of society, for educational re-orientation and above all for banishing war may stay. We welcome them. But we insist on a clear psychological orientation for all of them. The planning committees must have their angle of vision altered so that they may see clearly the psychological components of the social forces they are trying to marshall in the service of their plans. Seeing these forces they must use them as foundations for all their schemes of national welfare. Often they will find that their plans carry astray, and that their intentions are frustrated. They will feel exhausted in their efforts to stem the tide threatening to overwhelm their plans. It is then that psychological knowledge will prove a strong and trusty staff to lean on. They must seek this knowledge at least for the purpose of controlling and directing the enormous mental energy of the numerous operatives who will have to work out their plans.

The first step, therefore, and it may seem strange to many, that I would prescribe for the attainment of happiness, is the organisation of extension lectures and laboratory training in depth psychology and applied psychology for those who have to deal with groups, large or small, of men and women. Independent departments of Psychology will have to be brought into existence in all our Universities and made responsible for rendering this most important 'essential service' to the nation. Then, in the second place, a National Psychoanalytic-psychiatric Service affiliated to the All India Psychological Service mentioned in the previous paragraphs, and organised more or less on similar lines, should be brought into existence. In war time we realised the great value of the service rendered by the analytic psychiatrist in selecting recruits and in treating war neuroses. Our experience should convince us of the utility of preventive psycho-therapy in the daily life of



the 'civilised' citizen today. Our social structure just now is such as to favour the generation of psychic disorders. A careful objective study of the real events of history reveals to us the fact that nature attempts to draw mankind more and more together in ties of intimate social relationships. On the whole we *are* progressing towards social unity. But there is a bitter price to pay for achieving human solidarity in the shape of relinquishing the egoistical impulses. This price is heavy and is not easily paid. The conflict between the egoistic and social impulses is very acute at those critical times when man has to make a supreme effort to climb one more step towards unity, and it is at these times that psychogenic disorders are most common and dangerously infectious. The present is such a critical time and calls urgently for the curative and preventive measures of psycho-therapy.

We must begin our work in the nursery, carry it on to the school and finally extend it to cover the home, the place of business and of recreation and every other field of human activity. Child guidance clinics which are now few and far between should be organised on a nation-wide scale, and through these clinics arrangements should be made not only for treating the mental ailments of children but also for preventing them through the proper psychological education of parents and primary school teachers who are the 'villains of the piece'. Parents must be made to realise that children are not meant to be so many channels for draining off the energy of their complexes. The danger should be brought home to them of their unaided attempts to treat their own children for mental troubles. They should be encouraged to bring their mentally sick children to the clinics for treatment.

A very important duty which the child guidance clinics should take up at once is the psychoanalysis of elementary school teachers. It is now a well established principle of mental dynamics that sympathetic induction of emotions and sentiments operates both at the conscious and the unconscious levels of the mind. The teacher, without being aware of it, may infect the children under his charge with the ugly complexes hiding in his own unconscious. Let him be subjected to analysis, and let his unconscious be inoculated, and then the danger of infection will be considerably reduced. Not only teachers, but all those placed in charge of groups of men in any of walk of life should be inoculated psychologically in the manner prescribed by psychoanalysis. Here then is a most indispensable essential service for the nation which has yet to be created, and the need for whose creation is most pressing in the interests of individual as well as national welfare and happiness.

What, then, about parents? We are not neglecting them. In fact, we shall get at them before they become parents. We have spoken of the Children's branch of the All India Analytic Service. Of the Adult's branch of the same service, the marital section is a most important one. Before and after marriage, and also at the time of their early parenthood, life-partners will find it exceedingly profitable to consult the specialist who understands the dynamics of their unconscious. Your mind may be your own, just as your car is. But it goes without saying that driving blindfold will result in wreckage!

In addition to the marital section the Analytic Service will have Industrial, Political, Legal and other branches charged with the duty of handling the unconscious in these institutions organised for human welfare. Such an All India Service operating in close collaboration with the Psychological Service already mentioned, and other services contemplated by planning committees will secure for us an amazing amount of happiness which we are sadly missing today.



## EFFICIENCY AND HAPPINESS NOT THE BE-ALL AND END-ALL OF HUMAN LIFE

And now I take up the last and the most important aspect of the rôle which psychology has to play in reorganising human society. After efficiency has been secured through the instrumentality of applied psychology, and after an appreciable degree of happiness has been attained with the help of depth psychology, the question still remains, what does all this lead to? What is the final goal of human endeavours? Are efficiency and happiness ends in themselves, or only means to a supreme end beyond themselves? These questions have to be faced and answered, and *it is here that INDIAN PSYCHOLOGY comes in* to help us.

Granting that the psyche has been made hale and healthy through catharsis, sublimation and removal of repression, granting also that on the conscious level too harmony has been achieved between innate ability and the outer environment, the problem of the proper spiritual direction of human life still remains. The picture that I have drawn of the cleansing of the unconscious in the interests of sanity brings to my mind a famous parable of Christ. The haunted house has had the evil spirit driven out: it is swept clean, white-washed and made tidy. But there is no occupant. So, the erstwhile disturber of peace finding the dwelling very clean and neat and inviting, with no one on the premises to dispute its possession, goes and fetches seven more *ghostly* companions and enters the place riotously. That is exactly what will happen to the minds of individuals and nations if they halt at the middle goal of earthly happiness. They should push ahead and reach the highest goal of spirituality.

## THE TRUE GOAL OF HUMAN LIFE

The Hormic branch of depth psychology tells us how the germinal mental structure develops into sentiments, concrete and abstract, how these are organised into graded scales of values and how finally a permanent scale with a supreme master-sentiment or sovereign sentiment comes into existence. It is in the sovereign sentiment that we must look for our final goal. It is this pole star of life that should guide all our movements on earth. In the East as well as in the West, in ancient as well as in modern times, several master-sentiments have been tried and found utterly wanting. They have proved to be mere will-o'-the-wisps entangling man's feet in the morass of greed, lust and unholy passion for power. Society, state, nation and even humanity have been accorded at different times and in different places the seat of sovereignty in the mental scale, but sooner or later they proved to be so many quasi-divinities with clay-feet. They may be worthy of reverence as mere *dwarapalakas*, but unfit to worshipped as the supreme *ishla* of our life. And that supreme ideal is to be found in the *sanctum sanctorum* at whose gate-way the lesser ideals wait and watch as servants. It is none other than what our scriptures call PARA BRAHM. It is the realisation of this Para Brahm that is the highest goal of human life. In fact, there is no other real goal for us. Realising this supreme ideal, we realise our own true self.

The course of evolution of mental structure and function, as we have already noted, points to the master-sentiment as the goal for man. Now, there is one supreme test of the worth of any given goal of evolution. Does it, after it is reached, keep the mind still under the sway of the desires, passions and enslaving sentiments which belong to the lower stages of evolution? Does it keep the door open for the mind to regress to the lower levels



of attachment to objects of sense? If it does, then it is unworthy of pursuit as the supreme goal of life. If now we weigh all the pseudomaster-sentiments in our scale we shall find them woefully wanting in virtue. Para-Brahm-regard is the only goal that will pass our test.

Our own psychology prescribes this goal and also points the way to reach it. I shall merely enumerate the stages or steps prescribed by our spiritual psychologists for the attainment of the true goal of life. First comes *sraddha*, faith in divinity, then the company of holy men and *nishta*, concentration, meditation and prayer, then *ruchi* or taste for spiritual enjoyment, then *asakti* or attachment for the Lord, followed by *prema* or divine love and *mahabhava*, the final realisation. True, in this anti-spiritual age this may seem a formidable task for the masses. But those of us who are favourably placed and have command over others should follow this path. And the unique mental law of sympathetic induction will do the rest for the masses.

### CONCLUSION

Psychology, then, that is worthy of the name teaches us that in any scheme for the rehabilitation of society we should follow the natural course of evolution of the human mind. That course is from efficiency to happiness, and from happiness to self-realisation. The ascent of man is from knowledge to social service, and from this to the realisation of Divinity ; from *brahmacharya* to *grhastasram* and from this to *vanaprastha* and *sanyasa*. As I was writing these concluding sentences my mind conjured up an image of the noble path which humanity has to tread for salvation, in terms of the relative locations of the great institutions in my holy city of Prayag. The path runs from my University to Swaraj Bhavan, and from Swaraj Bhavan to the Shrine in the Bharadwaj Asram! From calm contemplation of truth to its testing in the service of society, and thence forward to the supreme joy (anandam) of Union with God-head! That is the path that psychology prescribes for all of us. This lesson I have learnt from my synthetic study of Eastern and Western Psychology, and I crave to pass it on to you in all humility and prayerfulness!







# FORTY-FOURTH INDIAN SCIENCE CONGRESS

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## SECTION OF BOTANY

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### PRESIDENTIAL ADDRESS

#### AIR POLLUTION IN RELATION TO PLANT DISEASES

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##### 1. INTRODUCTION

The measure of a country's progress is the amount of coal consumed for industrial purpose. With the march of civilization industries spring up, chimneys raise their lofty heads and smoke, the visible exhalation of the combustion product of coal, pervades the atmosphere. It is specially true for bituminous coals which are rich in volatile products and produce the largest quantity of smoke when burnt. Coal, the essential constituents of which are carbon, hydrogen, oxygen, nitrogen and sulphur, variously combined, on complete combustion produces carbon dioxide, water vapour, free nitrogen and sulphur dioxide ; the last named is rapidly converted into sulphurous acid and sulphuric acid. In incomplete combustion depending upon the nature of the coal, the product is tar, phenols, illuminant gas, methane, ethane, carbon dioxide, carbon monoxide, nitrogen, gaseous hydrocarbons and unsaturated hydrocarbons. The coal smoke thus consists of "unconsumed distillation products in association with carbon, tarry matter together with dust and ash".

The effluents from industrial plants pollute the atmosphere ; the extent of this can only be realised when we consider that amount of coal annually consumed in India is about 36,000,000 metric tons. On the basis of 2 per-



cent sulphur content of coal the total sulphur dioxide output in pure gas form is roughly 25,000,000,000 cu. ft. which represents a colossal figure considering that the gas at dilution of one part in a million can cause toxic effects in plants.

Air pollution is most serious in industrial towns. Usually diluted by wind current it spreads out without causing much visible harm either to plants or human beings, but under certain meteorological conditions, the effluent irritant gases unable to diffuse out, remain suspended in the atmosphere and cause enormous harm. Such was the condition in the Meuse Valley near Liege in Belgium in December 1930, when 64 persons died of respiratory disease. According to Roholin (1937) it was fluorine intoxication. Firket (1936) concluded that the noxious fumes were sulphur dioxide and sulphuric acid. In Donora (Pennsylvania) "stagnant meteorological conditions which confined smoke and waste fumes within the river valley caused 20 deaths and 100 hospital cases" (BYB 1949). "In winter of 1952 in the fog disaster of London some 4,000 people died within a fortnight; all age groups were affected, but specially those over 45" (BYB 1954).

It is these and similar incidents that focus our attention to the gravity of air pollution as a danger to national health, and as the special committee set up by the British Government stated that "the air pollution in the scale we know today is a social and economic evil and must be combated with the same conviction as was applied 100 years ago in securing pure water" (HMSO 1954).

Besides, atmospheric pollution has a profound influence on the vegetation. Frings (1930) states that formerly flourishing forests on the north edge of the Ruhr are dying out as a result of fumes of industrial plants; broad leaved trees affected by fumes even if not killed, become ready victim to fungi and insect pests. Similar smoke damages have also been recorded from other countries. In Canada, the damage to vegetation on account of fumes from the Smelter at Trail, started an international dispute, which brought the problem of sulphur dioxide injury to prominence (NRC 1939). Sulphur dioxide has been the source of litigations in other countries as well. Air pollution has serious effect on agriculture. It destroys growing crops, decreases their yield, damages vegetables, green house plants, flowers and nursery stocks. Middleton *et al* (1950) recorded the shifting of the location of operation by certain producers to areas free from gaseous effluence. The air pollution thus becomes a national problem.

The interest in air pollution follows the trend of industrialisation. The older works dealing with air pollution are from Europe. Most of the early literature originated there. It is comparatively recently that interest has gained momentum in U.S.A. Intensive researches are in progress in several centres on various aspects of air pollution and within a short period many important publications have appeared.

I propose to outline here today our present knowledge of air pollution in relation to plant diseases and shall briefly refer to certain aspects of these problems in India, which assume special significance in view of the increasing threat of air pollution from national programmes of industrial expansion. The problems arising from radioactive air pollution are beyond the scope of this survey and shall therefore be omitted from our present discourse.

Air pollutants are present in the atmosphere in three different phases : (1) gaseous phase, (2) aerosol phase which comprises an aerial dispersed system consisting of particles varying in diameter from  $0.01-50 \mu$  and



(3) particulate matter. Of these, the gas phase is more common and widely distributed and is the usual toxic phase. Aerosol phase appears during the periods of foggy weather when moisture drops dissolve the toxic gases. The particulate matter released in atmosphere, while by itself non-injurious, may help in the formation of aerosol (Middleton *et al* 1950).

The reaction of some susceptible species to minute quantities of gas is remarkable—for example, gladiolus var. Shirley Temple is sensitive to fluorine in one part per billion and at a lower concentration (0.1 ppb.) in longer exposure (Compton and Remmert cited by Thomas 1956). Similarly tomato plant is affected in a concentration of ethylene in one part in 100 million, and also shows extreme sensitivity to the presence of traces of phenolic compounds (2,4-D groups) in the atmosphere (Zimmerman 1952). Plants showing this property are being utilised as test plants in order to detect the gases present in infinitesimal quantity in the atmosphere, which can hardly be analysed by any known physico-chemical method. The choice of a test plant will depend upon its specific reaction to a gas; thus gladiolus for fluorine, tomato for ethylene. Test plants must necessarily be young, healthy and most vigorously growing. This ultra-sensitiveness of many plants to minute doses of gases and newly developed compounds may open up problems in agriculture.

The plant diseases caused by air pollutants are not systemic. The symptoms of injury are chlorosis and lesions which appear as spots and markings in the susceptible parts of plants. The susceptibility of the organs with reference to a particular gas is specific. In the case of sulphur dioxide, hydrofluoric acid, chlorine, indeed in most of the industrial gases, usually only the leaves are affected. The spotting and markings take place, and in severe cases of injury there is an abscission of the leaves. In susceptible varieties, at a long exposure stems are also affected. In the leaves it is the margin, tip and intercostal tissue which are more susceptible; the veins are injured only at a late stage. In flowering condition the injury may extend to petals and to awns in grasses. It is only ammonia which produces discolouration of the general surface of the leaves.

The effects of illuminating gas and its components, ethylene, carbon monoxide and hydrocyanic acid are different. The injury in trees may appear in different forms in roots, shoots and leaves; herbaceous plants can be defoliated, buds destroyed and actively growing shoots killed.

In evaluating the symptoms from the field studies, care should be taken to distinguish them from injury due to fungi, insects, nutritional disorders, drought and other physiogenic diseases. In fact it is suggested (Bredemann and Radeloff 1937) that final proof of gas injury is the chemical analysis to show the excess of the gas in the affected parts.

For convenience in discussion I shall now take up with you separately the plant disease problems arising from the effects of (a) industrial gases, (b) smog and (c) brick-kiln fumes.

## II. INDUSTRIAL GASES

### SULPHUR DIOXIDE

Various industrial gases have significant effects on plants. Sulphur dioxide is one of the commonest gaseous products of industrial plants and one of the most toxic. Its study dates back to 1850 (Stoeckhardt). Earliest detailed work is by Schroeder and Reuss (1883) who accurately described



the injuries in conifers and deciduous trees. Since then the effect of sulphur dioxide on vegetation has been intensively investigated and several accounts are available of which publication of Canadian National Research Council (1939) is most comprehensive dealing exclusively with sulphur dioxide.

The characteristic symptoms of sulphur dioxide injury are well recognised. Broadly speaking the symptoms are chronic and acute. The chronic symptoms are found in leaves long exposed to gas in sublethal doses. The green colouration in interveinal portion changes to yellow. In acute symptoms the markings are marginal, intercostal and veinal. It starts as an watersoaked area, later assumes ivory colour or in some cases brown or brownish red. In cereals the leaf tips become red, then yellow, lastly white; when flowering the awns are bleached. In barley, banded, mottled and kill-back types of symptoms have been distinguished (Katz *et al*, 1939).

A wide variety of species are affected by sulphur dioxide and indeed it is doubtful if there is any which is completely resistant to its effects. Species as also varieties within a species greatly vary in their susceptibility. Plants arranged in the decreasing order of susceptibility to sulphur dioxide injury, as given by O'Gara, are alfalfa, barley, sweet pea, bean, oat, clover and wheat followed by cauliflower, tomato, cabbage and grape; the most resistant are apple buds and apple blossom (Thomas 1956, 9-8).

Among the plant parts, the leaf buds and developing leaves are most resistant and among leaves the middle-aged ones are most sensitive followed by older and then youngest leaves (Zimmerman 1949).

The susceptibility to sulphur dioxide increases over 40°F, below which the plants are resistant. The atmospheric sulphur dioxide absorbed by the soil does not injure the plants; on the other hand it improves the plant growth in such soil where sulphur is not present in optimum condition.

Sulphur dioxide in a concentration one part per million may cause typical symptoms in leaves when fumigated for a few hours. 0.04 ppm. is the minimum concentration which alfalfa leaves are affected in short exposure (Zimmerman 1949).

The toxic effect of sulphur dioxide on mango fruit has been investigated by Ranjan and Jha (1940), Sen *et al* (1943), Das-Gupta *et al* (1941), and Verma (1952). The objective in all these cases was mainly confined to the production of 'necrosis' or 'black-tip' disease in mango fruit, and does not refer to the effect on other parts of plants. Sen *et al* exposed mango fruits on trees confined in glass jars to 0.5, 1.0, 2.5, 10.0 and 100 percent concentrations of sulphur dioxide for varying period. Exposure lasted 1-10 minutes for 100 percent and 1 to 3 hours for other concentrations; some received intermittent treatment with 0.5 percent of gas. Das-Gupta *et al* exposed Safeda mangoes to very low concentrations of sulphur dioxide in a glass chamber specially designed for the purpose. The problem was reinvestigated by Verma with improved technique for administering minute doses in continuous current with variously designed apparatus by Datta (1944), both for mangoes on trees and for plucked mangoes. Sulphur dioxide was found to produce lesions in concentration of 46 : 10,000 in 20 to 30 minutes depending upon the mango variety tested. The mangoes of the size of the pea were more sensitive than the mangoes of  $\frac{1}{2}$ " length. Sulphur dioxide produced brick-red lesions round the lenticels on general surface of the fruit. Heavy doses produced large brown patches through the coalescence of these lesions. At lower concentrations, the number and size of lesions per unit area were roughly proportional to the concentrations



of sulphur dioxide administered in a given time. At still lower concentration, 4:10,000, fruits showed chlorosis and shrinkage of tissues at the tip. The histopathological study showed that in the affected region epidermal cells lost chlorophyll, the starch grains became less in mesocarpic cells, cell walls were coloured brown, and light brown deposits appeared in cell cavities. The affected area was delimited by the production of cambium tissue which produced cells which were ultimately suberised (Das-Gupta and Verma 1941).

## FLUORINE

Fluorine damage to vegetation, known for a long time near industrial plants, has in recent years gained much prominence as apart from causing foliage injury, it causes fluorosis of cattle and sheep feeding upon them. Fluorine in the atmosphere is present in the form of hydrogen fluoride, silicon tetrafluoride and fluosilicic acid.

Fluorine injury has been reported in the neighbourhood of aluminium, copper, iron, glass, brick, superphosphate and other chemical factories. Fluorine emitted by these factories is either directly absorbed by the plants or through the soil. The fluorine in air even in areas where gas injury is seen has an average less than 0.05 ppm., although leaves growing in the damaged area contained very high concentration of fluorine viz. 500 ppm.—1000 ppm. In soil fluorine is present in a larger concentration. Plants growing in soil rich in fluorine, have many times higher content of fluoride in their roots than in the leaves, but when fluorine is absorbed from the atmosphere, it is the leaves that contain a much higher concentration. In either case because of translocation the fluorine content of leaves is never inconsiderable.

Symptoms of injury caused by fluorine depend upon the susceptibility of host and in this respect there is a wide range of variation among the different species. Even there are intervarietal differences in susceptibility. In a given susceptible variety the symptoms vary with the concentration of gas employed. In very low fluorine concentration, one part per billion, on long exposure, gladiolus develops ivory-white or brown necrosis, the earlier symptoms being the water-soaked areas developing in the tip of the leaves. In higher concentration, one part per million, acute markings occur in the marginal and intervenial regions of the leaves, which are comparable to typical sulphur dioxide markings. In fact, sometimes they are indistinguishable in appearance.

In apricot and prunes the margin of the leaves first becomes yellow, then brown followed by necrosis of the tissues and the abscission of leaves (De Ong 1946 ; Miller *et al* 1948). In a heavily affected orchard about 50 percent of the injured leaves may be abscised. Fluorine injury of fruits in which apical part is affected has been recorded by Neger (1919) for apple by Kotte (1929) for plum and Radeloff (1939) for pear. In corn the symptoms are somewhat different. A low concentration of fluoride produces a chronic mottled type of injury followed by slight collapse of the tissue. The injury spreads over an extensive area of leaf and is not confined to tips and margins only (Thomas 1956).

A wide range of species are affected by fluorine. Some of these are arranged in order of their susceptibility, viz. gladiolus, pine (young needles), azalea, Italian prune, corn, peach, grapes, iris, and most resistant are pine (old needles) followed by citrus, zinnia and rhododendron (Thomas 1956, 9-23).



Unlike sulphur dioxide injury there is a time lag between fumigation and the development of the disease which is due to the time taken for the translocation of fluoride from the seat of absorption to the tip and marginal regions where the fluoride accumulates. The absorption of fluoride from the soil and its translocation to the leaf and also its exhalation into external atmosphere as observed by Zimmerman and corroborated by air analysis are intimately connected with the accumulation and ultimate injury.

### ILLUMINATING GAS

Illuminating gas when present in soil in a large quantity greatly disturbs the metabolism of plants inducing various kinds of abnormal tissue formations in stem and root (tubercle) and in some cases causing outright killing (Stone 1906, 1913; Doubt 1917; Harvey and Rose 1915).

On aerial exposure flower buds of carnation fail to open at a very low concentration of illuminating gas (1 ppm.); at a higher concentration actively growing rose shoots, bud shoots of carnation and flower buds of lily were killed, and there were also stunting effects, defoliation of rose buds and rolling and curling of leaves (Wilcox 1911; Zimmerman *et al* 1930, 1931-a).

The illuminating gas injury of aerial organs is mainly due to ethylene. It has been shown that in rose plants the effect of the two are essentially similar, only ethylene produced injurious effect (epinasty) at a much lower concentration (1:3,000,000) against that of the illuminating gas (1:10,000). Ethylene constitutes 3 per cent of the total gas. The injury to roots, however, is due to hydrocyanic acid as shown by the loss of soil toxicity with disappearance of the acid (Hitchcock *et al* 1934).

### ETHYLENE

Ethylene which has an important effect on plant metabolism, is also toxic at a relatively high concentration. The characteristic symptoms of ethylene injury are yellowing along veins from base to midrib followed by abscission, interference with elongation of shoots, the premature opening of flower buds and early fall of petals (Zimmerman *et al*. 1931-a). Contrary to the finding of Zimmerman, Shull (1930, 1931) reported loss of vigour in ethylene treated plants, notwithstanding the initiation of a large number of shoot primordia. The relation of temperature to disease development was found when no injury occurred below 50°C.

Ethylene stimulation induces the formation of intumescences under a wide range of biological conditions. The minimum concentration in which intumescence is formed is one part per hundred millions on a long exposure, but more readily when the concentration is increased to one part per million. Temperature exerts a marked influence on the number and size of intumescences; the optimum temperature for their formation is 15°C and the maximum is 30°C. Part of the same individual tree, the humidity and light have no influence in the absence of oxygen nor in the presence of 25 percent or more carbon monoxide (Wallace 1926, 1927).

The toxic effect of ethylene on mango fruit has been investigated by Ranjan and Jha (1940), Sen *et al*. (1943) and Verma (1952). Sen using 1.0, 5.0, 25.0 per cent pure ethylene on mango fruit found that pure gas has no effect whereas dilute gas turns the skin of the fruit yellow and produces deep brown or black lesions under the skin, fruit becomes soft and drops out subsequently. Verma using the improved continuous current apparatus



obtained results different from those of Sen and found that under laboratory conditions ethylene concentrations of 3 in hundred thousand to 5 in hundred thousand parts of air have no effect. At 1 in ten thousand, induced ripening and changed the green colour to yellow ; heavier concentration induced lesions as well as ripening ; and 12 parts in ten thousand rendered skin coat loose accompanied by formation of large brown patches on skin.

#### CARBON MONOXIDE

The toxic effect of carbon monoxide on plants was demonstrated by Richards and McDougal (1904). The effect at a higher concentration expressed itself in the retardation of stem elongation, differentiation of primary tissues and chlorophyll formation. There is the production of abnormally small leaves of normal shape, yellowing and their abscission. Formation of hypertrophied tissues in stem and root of most species has also been recorded (Knight and Crocker 1913 ; Zimmerman *et al.* 1933, 1933-a). Lower carbon monoxide concentrations evoked physiological responses, such as rooting, stimulation of older stem primordia, epinasty of leaves, growth vigour, loss of sensitiveness to external stimuli and behaved like an anaesthetic (Zimmerman 1935).

Das-Gupta *et al.* (Ann. Report 1941) and Sen *et al.* (1943) employed carbon monoxide in various concentrations to ascertain its toxic effect on mango fruit, with particular reference to the production of 'necrosis' or 'black-tip' disease of mango. The results obtained by both are essentially similar. Sen *et al.* exposed fruits of *Aman Dasher* variety of mango for 72 hours at 1 percent, 5 percent and pure carbon monoxide and observed that in 1 per cent concentration fruits were completely unaffected, at 5 percent very slight paleness was visible, but no change thereafter, whereas in pure carbon monoxide skin became yellow and fruits remaining hard persisted on tree and showed retardation in growth.

#### CHLORINE

Injury due to chlorine is rare in nature although it is much more reactive than even sulphur dioxide. The characteristic symptoms are marginal and interveinal injury which starts as water-soaked areas, turning brown and in more severe attack followed by abscission. In sugarbeet the upper epidermis may be affected giving it 'silver-leaf' appearance. The symptoms resemble those of sulphur dioxide rather than hydrogen fluoride. Minimum dose for a very susceptible test plant was 0.46 ppm. (Thornton *et al.* 1940). The investigation of Zimmerman (1949) exposing chlorine to a wide range of species showed that at 0.46 ppm. buckwheat (*Fagopyrum esculentum*) is affected in 1 hour ; at a higher concentration, 1.3 ppm., bean and radish take 30 minutes to show the symptoms and peach 3 hours at 0.56 ppm.

#### HYDROGEN CHLORIDE

Hydrogen chloride had been the cause of damage to vegetation when the gas produced as a by-product in Leblanc soda process was allowed to pass out in the atmosphere. Since the recovery of the gas was started it has ceased to be a problem (Thomas 1951). Hydrogen chloride is less toxic than sulphur dioxide. The lesions principally are marginal, interveinal or on tips of leaves. These are not distinguishable in appearance from sulphur dioxide injury (Thomas 1951).



## HYDROGEN SULPHIDE

Toxicity of hydrogen sulphide is the least and effective dose is between 40-400 ppm. Typical symptoms are scorching of leaves, resulting in ultimate death. Youngest leaves are most sensitive while mature actively functioning leaves were uninjured, which is contrary to the action of other gases (Thornton *et al.* 1940). Most susceptible plants were cosmos, radish, tomato, cucumber, while most resistant species are coleus, peach, strawberry, apple and carnation (McCallan *et al.* 1936).

## AMMONIA

Ammonia is less toxic than sulphur dioxide. Otto (1928) described ammonia injury to spruce in which needles turned pale green, then nearly white and finally red. The bark and wood of exposed side died out followed by the death of the tree. In tomato, sunflower and similar plants ammonia produces discolouration of the general surface of leaf "changing from green to cooked green finally brown upon drying". Concentration of 8.3 ppm. of ammonia seems to be threshold value for causing toxic effects in some plants (Thornton *et al.* 1940).

## NITRIC OXIDES

Plants exposed to a weak concentration of nitrous gas under a bell jar for 15 minutes to 18 hours produced some lesions at longer exposures. Symptoms are marginal browning and brown spots on leaves (Christiani 1927). The blades of cereals and needle-tips of conifers showed bright yellow colour. Nitrogen oxides are important as reacting with atmospheric unsaturated hydrocarbons they may produce smog.

## III. FACTORS INFLUENCING GAS INJURY

The injury of plants due to gas is directly proportional to the amount of gas absorbed. This absorption is the function of the general leaf surface or the stomata. Whether the absorption of sulphur dioxide is through general surface in which stomata plays no important role (Haselhoff and Lindau 1903) or the gas enters through the stomata (Janson 1937) or both (Verplancke 1927) was settled when it was demonstrated that absorption is controlled by stomatal aperture, a view which is now generally accepted (Thomas *et al.* 1935). By determining the physiological condition of the plant within the general condition of maturity, the environmental factors on the other hand influence the movement of the stomata and thereby the entry of the gas into the leaf.

The age of the plant subject to gas exposure thus plays a significant part in gas absorption. It is seen that usually the older plants which are most susceptible to gases and the youngest plant most resistant (Setterstrom *et al.* 1939) but there are also cases where young plants are more susceptible than the old (Widstoe 1903).

Again full grown and highly functional leaves are more susceptible than the old leaves and the young ones are more resistant when exposed to sulphur dioxide, hydrogen fluoride, chlorine and other gases except for hydrogen sulphide in which the youngest parts of the plants and leaves and rapidly elongating tissues are most susceptible (Hill *et al.* 1933 ; Setterstrom *et al.* 1939).



Among the environmental factors temperature plays a well-defined role in gas absorption. It shows particularly for sulphur dioxide, that plants growing below 40°F are most resistant (Swain 1923). There is an indication that above 100°F the plants may be more resistant (NRC 1939). Within this range there is no significant difference in absorption due to temperature variation. In mango necrosis the earlier phase of the development of fruit and the incidence of necrosis occur at a time when the atmospheric temperature in Lucknow is over 100°F and the main development of necrosis as well as the fruit takes place when temperature ranges between 105°F to 115°F.

The minor variations in soil moisture and humidity have no effect on the susceptibility of plants, but when the moisture content of the soil is reduced to the critical level of wilting, the resistance increases. The near-wilting condition decreases the turgidity of leaf cells effecting the closure of the stomata with consequent decrease in absorption. In mango necrosis the susceptible trees highly irrigated with water showed no discernible change in the number of diseased fruits (Das-Gupta *et al.* 1941-1951). Atmospheric humidity within a wide range has little effect on the absorption of gas.

Since stomata close in the dark checking the entry of the gases, plants grown in complete darkness are more resistant than those growing in light. It is for the same reason that an individual plant is more resistant at night than in the day and in cases where stomata do not close in the night, such as in potato and alfalfa, the resistance at day and night is the same. Plants grown in reduced light before fumigation are also more resistant.

The plants with deficient supply of nutrients proved to be more susceptible. In mango necrosis somewhat similar results have been obtained, not by manurial treatment, but by branch injection of Knop's nutrient solution. Intensive spray of diseased trees with borax showed that the disease advance and perhaps also incidence was greatly checked (Das-Gupta *et al.* 1940-1951).

#### IV. SMOG

Smog, a mixture of smoke and fog, appears in industrial cities where a large amount of organic and inorganic pollutants produced by the burning coal gas and other fuels pervade the atmosphere. Under certain meteorological conditions it may not have fog as its constituent, and then it is known as smog gas. The constituents of smog occurring in Los Angeles are sulphur dioxide, ammonia, oxides of nitrogen, sulphur trioxide, aldehydes, filterable oils, soluble chlorides, carbon, ozone, hydrogen sulphide, traces of minerals, organic peroxides, acrolein, fluorides, methyl chloride, formic acid, sodium chloride and gaseous hydrocarbons. Sulphur dioxide and fluorides are also present but in subtoxic concentration (Middleton *et al.* 1950).

The smog is usually present in the atmosphere to a greater or less degree, but when there is an accumulation and increased concentration of pollutants, the smog damage appears.

The symptoms of smog injury in plants are different from those characteristic of sulphur dioxide and fluorine injuries. The characteristic symptom due to gaseous component of smog (smog gas) is a glazed appearance on the undersurface of the affected leaves; in some there is bleaching developing into light-tan necrotic area. The glazed appearance is due to the collapse of mesophyll cells and their replacement by air in the inter-



cellular spaces. In severe attack scorching and necrotic spots appear involving entire leaf.

When smog is associated with heavy fog (smog fog) moisture is deposited on leaves as minute droplets which are somewhat acidic in character (acid aerosols). The deposits in contact with the leaf tissue produce leaf spots which advance progressively from upper surface to lower surface and ultimately develop into shot holes. No glazing or bleaching appears in these leaves. Similar injury is found to be produced by ozone (Haagen-Smit 1952a) which sometimes is a smog component.

As with other gases, the different species of plants show different degree of susceptibility to smog damage and some of them are named here in order of decreasing susceptibility. Endive, spinach, lettuce, barley, alfalfa. Most resistant is wheat followed by squash and rhubarb.

The nature of the smog agent was unknown till recently when the work of Haagen-Smit *et al.* (1952-a) and Koritz and Went (1953) appeared. Haagen-Smit (1952-a) while determining the compounds producing typical smog damage has shown that "the reaction product of ozone with unsaturated hydrocarbons produced typical smog damage on all the indicator plants. The damaging factor must, therefore, be attributed to the peroxides formed in the ozonization process". They were thus able to show that the vapours of some unsaturated hydrocarbons when combined with ozone or nitric oxide form a synthetic smog which causes plant injury identical to natural smog damage. Hydrocarbons which are normally non-toxic thus combined with another substance become very toxic. On the basis of this Koritz and Went (1953) prepared synthetic smog in the laboratory (1-*n*-hexene plus ozone) with a view to study the physiological action of synthetic smog on tomato plants.

Smog has been found to have retardation effect on growth of tomato plant (test plant) only when fumigated in light at midday or early afternoon. Fumigation in the dark or light following a 12-hour dark period or in the dark after 1½ hours of light had no smog effect. Koritz and Went (1953) also proved the presence of invisible injury due to synthetic smog.

Smog damage to plants, though not as extensive as that caused by irritant gases such as sulphur dioxide, fluorine and other industrial fumes, is nevertheless in several ways more important due to its effect on human health and of the invisible injury to plants caused by it.

## V. INVISIBLE INJURY

Some workers consider that long exposure of sulphur dioxide at sub-lethal doses causes invisible injury to plants, in which the plant does not suffer damage externally, but there is a reduction in the growth and reproductivity due to the interference of the gas in the assimilatory process. The view gained prominence and was debated during the early phase of the work on sulphur dioxide (Schroeder and Reuss 1883; Sorauer and Raman 1899). It has been revived by Stoklasa (1923) supported by several workers (Haselhoff *et al.* 1932; Jansen 1936, 1937). No experimental evidence has, however, been put forward to substantiate the view. The experimental evidence put forward by Swain and Johnson (1936) showed that wheat plant grown in otherwise optimum condition, on long exposure to sulphur dioxide, failed to show any reduction in yield. This finding was substantiated by Katz *et al.* (NRC 1939) for alfalfa. The photosynthetic and respirational studies by Thomas and Hill (1937) proved that "yield is a linear function of the extent of leaf area destroyed", and



no depression in assimilatory process occurs in the absence of visible damage. An extensive experimental study of alfalfa under different growth conditions exposed to sublethal concentrations of sulphur dioxide did not show any adverse effect (Setterstrom *et al.* 1938).

Recently, however, the question was reopened when Bleasdale (1952) working with a strain Aberystwyth 23 of *Lolium perenne* L. (rye grass) grown under controlled glass house conditions and exposed to polluted air of Manchester, found no trace of leaf damage, but "the treatment with purified air gave, with one exception, a dry weight considerably higher than treatment with polluted air". Koritz and Went (1953) investigating the physiological action of synthetic smog found a similar result on the growth of tomato plants. They demonstrated that synthetic smog may retard the yield of tomato plant without showing foliar markings or reduction in its photosynthetic tissue and stated that hidden damage or invisible injury as caused by smog may be widespread affecting many urban areas. It has been further suggested by Koritz and Went that it is very likely that 'Bleasdale effect' was due to some phytotoxic substances related to smog as found by them.

The present position, therefore, is that invisible injury is not caused by sulphur dioxide or most other similar gases, but it is caused by smog.

## VI BRICK-KILN FUMES

Brick-kiln fumes are the incomplete combustion product of coal at a comparatively low temperature, and to a certain extent mixed with the volatile substances present in the soil from which bricks are made. The fume constituents, although not fully worked out, comprise sulphur dioxide, ethylene, various hydrocarbons, and some tarry substance in unknown proportions. The fumes produce a disease of economic importance known as 'necrosis' of mango fruit (*Mangifera indica* L.), also designated as 'black-tip' because of the characteristic final symptom of the disease. The disease occurs near operating brick-kilns (Das-Gupta *et al.* 1939 ; Pal *et al.* 1937 ; Sen *et al.* 1941).

Necrosis invariably appears at the tip of the fruit ; the first external symptom is aetiolation of the apical region followed by small greyish spots which coalesce to form a continuous necrotic area of dark brown colour. Due to the disintegration and collapse of the epicarp and mesocarp tissue, stone emerges and remains protruding beyond the healthy flesh giving the characteristic final phase of the necrosis. In recent years, a variation of typical necrosis called 'girdle necrosis' has been discovered by Rai (1952). In this, the focus of necrosis is usually in the sinus region and there is usually more than one focus ; the final symptoms are indistinguishable from typical necrosis.

The internal symptom of necrosis is the presence of certain deposits in vessels and later on both in vessels and ducts. The deposits in the initial stages are fluid light-yellow, which passing from viscous deep yellow to semi-solid and solid brick-red types, ultimately become solid and dark brown in colour. The presence of deposits in the vessels is the first internal index of the disease (Das-Gupta *et al.* 1955).

The experimental fumigation with coal gas has produced typical necrosis in a number of fruits of a susceptible variety (Sen 1942-43). Similar investigations by Das-Gupta *et al.* (1944, 1951) were only partially successful as number of mangoes developing necrosis was small. The disease was, however, successfully produced by injection of sterile extract



from diseased tissue (Das-Gupta and Venna 1940). The fumigation of mangoes with the fume constituents, sulphur dioxide, ethylene and carbon monoxide separately, as stated elsewhere proved unsuccessful.

Isolation from the brick-kiln fumes of a certain crystalline substance which when injected into the mango fruit produces typical necrosis is of great interest (Das-Gupta *et al* 1950). The substance is as yet unidentified; and its isolation in extremely small quantity makes it difficult to ascertain its effect in fruits without direct injection.

There was some indication that nutritional deficiency plays a part in the development of mango necrosis. When Knop's nutrient solution was applied to the tree with branch injection, in about 70 per cent of the fruits the earliest stages of the disease were checked. Spraying borax and boric acid solutions on fruits showing the early stage of necrosis checked the further advance of necrosis and the incidence was minimised (Das-Gupta 1950 Ann. Rep., Das-Gupta and Sen 1956). There is so far no further record from India of injury to vegetable and other crops due to brick-kiln fumes, though an intensive study using test plants is most likely to reveal cases of incipient or visible smoke injury, particularly in view of the fairly significant sulphur dioxide content (47:100,000 parts of air) of the orchards situated at a quarter mile distance from the fume source (Verma 1952). The vegetation near the industrial centres too should similarly reveal injuries effect and it deserves careful investigation.

## VII. DIAGNOSIS OF AIR POLLUTION INJURY TO PLANTS

From the foregoing observations it would be clear that in a large majority of cases, injury suffered by plants due to air pollutants is expressed in the form of foliar damage. In more acute conditions, the young shoot tips and developing buds may be affected and there are also records of fruit tip injury in apple (Neger 1919), plum (Kotte 1929), pears (Radeloff 1939) and mango (Das-Gupta and Verma 1939). Apart from this, in the case of smog, the plants suffer from invisible injury also. Precise diagnosis of air pollution injury to plants is, however, beset with many practical difficulties. Symptoms caused by gas exposure often simulate those resulting from other types of disorders arising from causes physiogenic (drought, frost, winter injury and nutritional unbalance, etc.) and pathogenic (viruses, bacteria and fungi). It is thus necessary to distinguish between them. This problem has been dealt with at some length by Massey (1952).

Symptoms caused by different gases vary, and a particular gas may evoke different symptoms depending upon the conditions of exposure and the species, or even variety, affected. Several workers have carefully investigated the symptoms caused by individual gases under field and experimentally controlled glass-house conditions, using a wide range of species of plants, including conifers, fruit trees, cereals, vegetable and forage crops, ornamental and green house plants, belonging to both monocot and dicot groups, and distinguished as herbaceous, woody and broad-leaved forms. The plants at different stages of maturity have been studied under exposure to very minute (0.01 ppb) to much higher concentrations of gases, and various conditions of light, temperature, nutrition, relative humidity and soil moisture. The symptom complex shown by a particular species has been worked out, making it possible to diagnose gas injury with a fair degree of accuracy. But even with this detailed knowledge of symptomatology it is difficult to confirm the diagnosis. This has been emphasized by Katz (NRC-1939) in the following words:



"Within a given smoke zone, however, there is usually formed a wide variety of makings which may be caused by other factors such as drought, frost, winter injury, insects, disease and various physiological disorders. Accurate diagnosis of the distribution and degree of injury is, therefore, a difficult matter unless some knowledge is available of the character and intensity of gas visitations, the meteorological conditions, the sulphur content of the affected plant, and the reaction of susceptible indicator plants. The careful investigator must, therefore, utilise as aids in the diagnosis and estimation of injury, such knowledge as may be available by a study of factors enumerated above".

Once the air pollution injury in a plant has been screened out from other disorders, the problem devolves itself to the specific identification of the pollutant responsible for it. As has already been mentioned earlier, the effluents from industrial sources contain a variety of pollutants including sulphur dioxide, fluorine, ethylene, hydrogen sulphide, carbon monoxide, chlorine, and other organic and inorganic substances, occurring in variable proportions. The composition of the effluents depends upon the nature of the coal or other fuels, and the nature of ore etc. employed in a particular industry. Sulphur dioxide content of the effluents increases when high-sulphur coal is used or during the roasting of sulphide ores. Fluorine compounds are commonly derived from impurities and are mostly found in the effluents from aluminium, copper, iron and superphosphate factories. The effluents of the various chemical industries have also different gas composition.

In diagnosing symptoms arising in a given smoke-pervaded region, the possible agency of several gases detected in the region is to be taken into account. For sulphur dioxide and fluorine, for example, Thomas *et al.* (1949) states that "the lesions due to hydrogen fluoride are somewhat similar in appearance to acute sulphur dioxide markings, but their location on the leaf is often different"; the difficulties attended upon evaluating the markings, however, have been experienced and pointed out by several workers. Thus for both sulphur dioxide and hydrogen fluoride, diagnosis based on symptoms alone is not always possible (Johnson, *et al* 1950). The position with regard to minor gases, such as chlorine, hydrogen sulphide becomes even more difficult. It is yet to be found out whether several gases present in sublethal concentration are able to produce any disease symptoms.

The use of 'indicator' or 'test' plants is another method of detecting the atmospheric pollutants in a given smoke-pervaded region. The method is based on the differential reactions of different species and varieties of plants to the commonly occurring gases. The ultra-sensitiveness of various species has given an impetus to this work and intensive investigation is in progress in various laboratories abroad, in which the susceptible varieties grown under controlled condition in an atmosphere in which the desired gases can be introduced in infinitesimal doses. As a result of such investigations the various species of plants have been divided into three different groups, susceptible, intermediate and resistant, for each of the three important toxic agents, sulphur dioxide, fluorine and smog by Thomas (1956). Differential reaction of test plants sensitive to the various air pollutants can be employed to detect the specific injury causing substance in the atmosphere and it may even be possible to utilise this technique for making a fair surmise of the pollutant concentration present there.

Symptoms alone, however, are not very reliable guides to the diagnosis of the disease or the detection of the presence of pollutants in air. Sympto-



matological evidence of air pollution injury in plants needs corroboration by other more objective techniques.

The chemical analysis of diseased tissue as a method of demonstrating gas injury has been suggested by Bredemann and Radeloff (1937). For the confirmation of both sulphur dioxide and fluoride injury chemical analysis of affected tissues has been taken up. Its value for sulphur dioxide injury, however, is doubtful. The sulphur content of leaves of plants exposed to sulphur dioxide has been found to increase substantially (NRC 1939). But while there is a correlation between sulphur content of leaf and disease production in certain cases, there is evidence that the visitation of a high concentration of gas may produce disease symptoms, finally death, without increase in the sulphur content (Johnson *et al* 1950). On the contrary, as pointed out by Katz (NRC 1939), the accumulation of sulphur in leaves of plants exposed to sulphur dioxide atmosphere may reach values more than three or four times the normal content without showing external injury.

The fluoride content of the tissues affected by hydrogen fluoride has received considerable attention. The absorption of fluorine from the soil and atmosphere, its translocation to the leaf margins and tips from the root, as also from the seat of absorption of the leaves, its accumulation and final volatilization, are peculiarities not shown by other gases causing injury to plants. Johnson *et al* (1950) pointed out that "physical appearance is not enough to distinguish fluorine injury to plants; the symptoms must be correlated to other facts, including an abnormally high fluorine content of the tissue".

Thus the result of the study of the fluorine content of air soil and the vegetation throws an interesting light on the problem of fluorine damage. Miller *et al* (1952) investigating the ponderosa pine blight where trees were injured by fluoride from an aluminium plant, found that whereas the area outside the influence of gas had needles containing 2-4 ppm of fluorine, within the affected area, the current year needles contained 129 ppm of fluoride and three year old needles as high as 462 ppm; the fluoride concentration of air being 0.064 ppm.

The fluoride content of the air near a superphosphate plant was found to be 0.029 ppm (Largent 1949). Near an aluminium factory, fluoride content in the vegetation ranged from 5 to 1000 ppm. The concentration is variable since the accumulation of gas effluents from the factories and that from exhalation of leaves depends upon the velocity of wind. High fluoride content of tissue may not always reveal the disease symptoms. There is a great difference in the ability of a plant to absorb and tolerate fluorine. Concentrations as high as 5000 ppm have been observed in uninjured cotton leaves (Thomas 1951).

Chemical analysis, therefore, though it may confirm the findings from other methods, cannot be used as a sole criterion unless tolerance value of each plant is known; this, then leads to the experimental production of the disease by suitable gas exposure.

Apart from chemical methods, physical techniques, though of limited value, have also been employed in the diagnosis of gas injury in plants. "Dorries (1932) has developed a method which although not specific for sulphur dioxide serves to detect injuries caused by acid gases. He believes that in case of acute injury, the acid gas acts directly on the chlorophyll, changing it into phaeophytin, through the splitting off of magnesium. The presence of phaeophytin from injured leaves was demonstrated by the use of spectroscope. Phaeophytin is not present in the case of autumnal colouration, or drought, frost and parasitic injury. It does not



arise also in leaves showing symptoms of chronic sulphur dioxide injury" (NRC 1939, p. 54). This method, if generally applicable, will be a handy tool for distinguishing sulphur dioxide injury from other physiogenic disorders in plants.

Recent work of Nielsen, Benedict and Holloman (1954) indicates the possibility of developing an objective method of assessing the responsibility of smog for vegetation damage. They found that when smog-marked leaves were irradiated with near ultra-violet light from a mercury vapour lamp, the marked areas appeared as sharply defined bright pale blue. As the markings caused by hydrogen fluoride, sulphur dioxide, hydrogen sulphide, chlorine, oxides of nitrogen, sulphur trioxide and ozone did not fluoresce under ultra-violet light, this technique may be used to distinguish smog injuries from those caused by other gases. Nielsen, Benedict and Holloman, however, have pointed out that care should be taken to distinguish the smog markings from pure white markings, produced at times with sulphur dioxide and chlorine, which readily reflect light and almost appear to fluoresce under ultra-violet. This is also true of the spotty white, granular injury produced by sulphur trioxide. Further as fungus hyphae and insect deposits also fluoresce blue, it is important to examine the leaves microscopically with visible light.

Criteria for confirmation of diagnosis of diseases produced by pathogenic organisms have been laid down by Koch. To some extent comparable criteria for diagnosis of air pollutant injury in plants seem to be desirable. I consider that (1) the presence of the pollutant in the air, (2) demonstration of distinctive tissue reaction in the plant by objective analytical methods, and (3) experimental production of the symptoms by suitable exposure to the air pollutant, may be collectively employed as criteria to confirm the diagnosis of air pollution injury in plants.

There is, thus, the need for survey, diagnosis and study of plant diseases caused by air pollutants. The pathologists and physiologists must necessarily experiment with new tools and techniques to unravel the various aspects of the problems of production and control of plant diseases arising from air pollution.

### VIII. CONCLUDING REMARKS

In a brief compass, ladies and gentlemen, I have attempted to unfold before you this morning, the broad aspects of the problems of air pollution in relation to plant diseases. The solution of problems arising from air pollution impinges on diverse fields of scientific endeavour and legislative action. Controlling at source of the pollutants produced as by-products of industrial processes; the elucidation of the physics and chemistry of the polluted atmosphere; the evaluation of the weather effects on air pollution epidemiology, are the work of the specialists in their respective fields of study. The aspect of the study of the human and animal health in the polluted atmosphere lie in the domain of medical and veterinary research. The problems of impact of air pollution on damage to vegetation embrace several spheres of botanical research involving concerted efforts of workers in pathology, physiology, ecology and also genetics where radio-active pollutants occur. I may, however, draw your attention to the paucity of records of air pollution damage to plants in India. It is difficult to conceive that the vegetation near industrial centres in this country is entirely free from air pollution damage.



India today is at the threshold of a new industrial revolution. Big development schemes have been launched under the two successive Five Year Plans. New industries are springing up and large factories, refineries and other industrial plants are being constructed in different parts of the country, increasing more than ever before the degree of air pollution and its consequent hazards to plant, animal and human health. Here is then a fruitful field of study, the fundamental aspect of which can hardly be equalled by its economic and social importance.

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